2017

AP® CollegeBoard

AP Chemistry

Sample Student Responses and Scoring Commentary

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Question 2

Answer the following questions about the isomers fulminic acid and isocyanic acid.

Two possible Lewis electron-dot diagrams for fulminic acid, HCNO, are shown below.

H—C≡N—Ö: H—C̈=N=Ö:

(a) Explain why the diagram on the left is the better representation for the bonding in fulminic acid. Justify your choice based on formal charges.

In the diagram on the left, the C atom has a formal charge of zero and the O atom has a formal charge of –1. In the diagram on the right, the C atom has a formal charge of –1 and the O atom has a formal charge of zero.	1 point is earned for a correct assignment of formal charges in the two diagrams.
The diagram on the left is the better representation because it puts the negative formal charge on oxygen, which is more electronegative than carbon.	1 point is earned for a correct explanation.

Fulminic acid can convert to isocyanic acid according to the equation below.

$$HCNO(g) \rightleftarrows HNCO(g)$$

fulminic acid   *isocyanic acid*

Fulminic Acid	Isocyanic Acid
H—C≡N—Ö:	H—N̈=C=Ö:

(b) Using the Lewis electron-dot diagrams of fulminic acid and isocyanic acid shown in the boxes above and the table of average bond enthalpies below, determine the value of $\Delta H°$ for the reaction of $HCNO(g)$ to form $HNCO(g)$.

Bond	Enthalpy (kJ/mol)	Bond	Enthalpy (kJ/mol)	Bond	Enthalpy (kJ/mol)
N–O	201	C=N	615	H–C	413
C=O	745	C≡N	891	H–N	391

Compound	HCNO	HNCO
Bond Enthalpies (kJ/mol)	413 + 891 + 201	391 + 615 + 745
Total Bond Enthalpy (kJ/mol)	1505	1751

$\Delta H° = \Sigma$(enthalpies of bonds broken) – Σ(enthalpies of bonds formed)
$= 1505$ kJ/mol – 1751 kJ/mol
$= -246$ kJ/mol$_{rxn}$

1 point is earned for subtracting the enthalpies of bonds formed from the enthalpies of bonds broken.

1 point is earned for the correct determination of $\Delta H°$.

Question 2 (continued)

(c) A student claims that $\Delta S°$ for the reaction is close to zero. Explain why the student's claim is accurate.

The change from fulminic acid to isocyanic acid is a rearrangement of atoms with no change in phase or number of molecules.	1 point is earned for a correct explanation.

(d) Which species, fulminic acid (HCNO) or isocyanic acid (HNCO), is present in higher concentration at equilibrium at 298 K? Justify your answer in terms of thermodynamic favorability and the equilibrium constant.

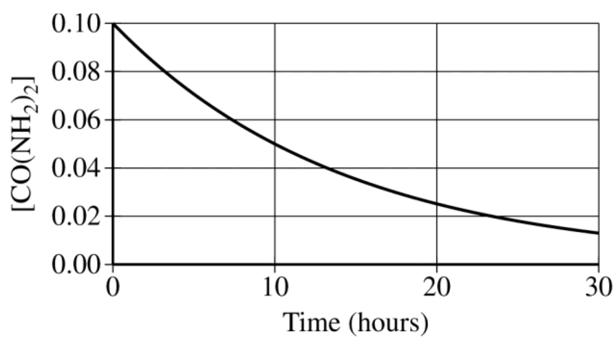
Isocyanic acid (HNCO) will be present in higher concentration. $\Delta G°$ is essentially equal to $\Delta H°$ because $\Delta S°$ is essentially zero, so $\Delta G° \approx -246$ kJ/mol$_{rxn}$, indicating the forward reaction is thermodynamically favorable.	1 point is earned for the correct choice **with** a valid justification. (Calculation of $\Delta G°$ is a sufficient justification.)
Since $\Delta G°$ is negative, $K > 1$ ($\Delta G° = -RT \ln K$), resulting in a higher concentration of product than reactant at equilibrium.	1 point is earned for correctly connecting thermodynamic favorability to the equilibrium constant, K.

The ammonium salt of isocyanic acid is a product of the decomposition of urea, $CO(NH_2)_2$, represented below.

$$CO(NH_2)_2(aq) \rightleftarrows NH_4^+(aq) + OCN^-(aq)$$

A student studying the decomposition reaction runs the reaction at 90°C. The student collects data on the concentration of urea as a function of time, as shown by the data table and the graph below.

Time (hours)	$[CO(NH_2)_2]$
0	0.1000
5	0.0707
10	0.0500
15	0.0354
20	0.0250
25	0.0177
30	0.0125



Question 2 (continued)

(e) The student proposes that the rate law is $rate = k[CO(NH_2)_2]$.

(i) Explain how the data support the student's proposed rate law.

From inspecting the data table or the graph, it is evident that the decomposition reaction has a constant half-life, which indicates that the reaction is a first-order reaction.	1 point is earned for a correct explanation.

(ii) Using the proposed rate law and the student's results, determine the value of the rate constant, k. Include units with your answer.

Since the reaction is first order, $k = \frac{0.693}{t_{1/2}} = \frac{0.693}{10.\ \text{h}} = 0.069\ \text{h}^{-1}$ OR $k = \frac{\ln[A]_0 - \ln[A]_t}{t} = \frac{\ln(0.1000) - \ln(0.0500)}{10.\ \text{h}} = 0.069\ \text{h}^{-1}$	1 point is earned for the correct value of k with correct units.

(f) The student learns that the decomposition reaction was run in a solution with a pH of 13. Briefly describe an experiment, including the initial conditions that you would change and the data you would gather, to determine whether the rate of the reaction depends on the concentration of $OH^-(aq)$.

Perform the experiment at a different concentration of $OH^-(aq)$ and measure how the concentration of $CO(NH_2)_2$ changes over time. (Other variables, such as temperature, should be held constant.)	1 point is earned for the description of a valid experiment.

2. Answer the following questions about the isomers fulminic acid and isocyanic acid. 2A 1 of 4

Two possible Lewis electron-dot diagrams for fulminic acid, HCNO, are shown below.

H—C≡N—Ö: H—C̈=N=Ö:

4−4=0 5−4=1 6−7=−1 4−5=−1 5−4=1 6−6=0

(a) Explain why the diagram on the left is the better representation for the bonding in fulminic acid. Justify your choice based on formal charges.

Fulminic acid can convert to isocyanic acid according to the equation below.

$$HCNO(g) \rightleftarrows HNCO(g)$$

fulminic acid   *isocyanic acid*

Fulminic Acid	Isocyanic Acid
H—C≡N—Ö:	H—N̈=C=Ö:

(b) Using the Lewis electron-dot diagrams of fulminic acid and isocyanic acid shown in the boxes above and the table of average bond enthalpies below, determine the value of $\Delta H°$ for the reaction of $HCNO(g)$ to form $HNCO(g)$.

Bond	Enthalpy (kJ/mol)	Bond	Enthalpy (kJ/mol)	Bond	Enthalpy (kJ/mol)
N−O	201	C=N	615	H−C	413
C=O	745	C≡N	891	H−N	391

(c) A student claims that $\Delta S°$ for the reaction is close to zero. Explain why the student's claim is accurate.

(d) Which species, fulminic acid (HCNO) or isocyanic acid (HNCO), is present in higher concentration at equilibrium at 298 K? Justify your answer in terms of thermodynamic favorability and the equilibrium constant.

The ammonium salt of isocyanic acid is a product of the decomposition of urea, $CO(NH_2)_2$, represented below.

$$CO(NH_2)_2(aq) \rightleftarrows NH_4^+(aq) + OCN^-(aq)$$

A student studying the decomposition reaction runs the reaction at 90°C. The student collects data on the concentration of urea as a function of time, as shown by the data table and the graph below.

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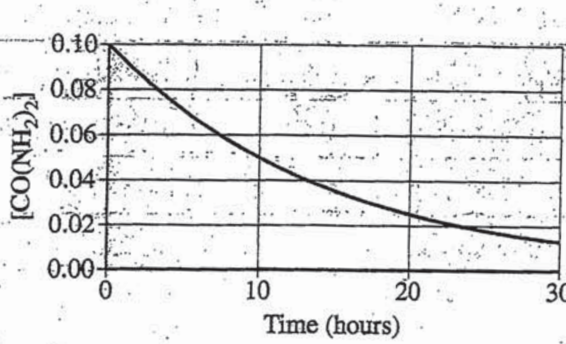

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(e) The student proposes that the rate law is $rate = k[CO(NH_2)_2]$.

(i) Explain how the data support the student's proposed rate law.

(ii) Using the proposed rate law and the student's results, determine the value of the rate constant, k. Include units with your answer.

(f) The student learns that the decomposition reaction was run in a solution with a pH of 13. Briefly describe an experiment, including the initial conditions that you would change and the data you would gather, to determine whether the rate of the reaction depends on the concentration of $OH^-(aq)$.

2) a. The diagram on the left is the better representation for the bonding of fulmanic acid. The left diagram designates ~~a~~ formal charges of 0 for hydrogen, 0 for carbon, +1 for nitrogen, and −1 for oxygen. This is appropriate since oxygen, the most electronegative atom, takes the negative/lowest formal charge and all of the formal charges are as close to 0 as possible. The second diagram doesn't work since even though oxygen is most electronegative, it takes a formal charge of 0 and ~~nitrogen~~ carbon takes the lowest formal charge at (−1). Note: ~~that~~ formal charge ~~equals~~ = # of valence e^- minus (1/2 # shared e^- ~~*~~ plus ~~#~~ # of unpaired e^-).

$H-C\equiv N-\ddot{O}:$ $H-C\equiv N=O:$

1−1=(0) 4−4=(0) 5−4=(+1) 6−7=(−1)   1−1=(0) 4−5=(−1) 5−4=(+1) 6−6=(0)

b. $\Delta H° = \Sigma$ bond enthalpy$_{reactants}$ − Σ bond enthalpy$_{products}$

$\Delta H° = (413\text{ kJ/mol} + 891\text{ kJ/mol} + 201\text{ kJ/mol}) - (391 + 615 + 745)$

$\Delta H° = -246\text{ kJ/mol}$

c. The $\Delta S°$ is close to zero since the entropy does not change much during the reaction. This is because the number of moles of the reactants used equals the number of moles of

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product created and the phase remains the same, maintaining a gaseous state.

d. $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$, and since the ΔH° is negative and the ΔS° is close to zero, the ΔG° will be negative. When the standard Gibbs free energy is negative, the reaction is spontaneous, meaning the foward reaction is favorable so $K > 1$. Thus, HNCO is present at a greater concentration at equilibrium.

e. i. The data supports this conclusion since the formula demonstrates that the reaction is first order with respect to $[CO(NH_2)_2]$ and the data demonstrates a constant half-life of 10 hours. First order reactions maintain the same half-life throughout.

ii. $t_{1/2} = .0693/k$ $t_{1/2} = 10$ hrs $10 \text{ hrs} = .693/k$

$k = .0693 \text{ hours}^{-1}$ [ANSWER: $\frac{0.0693}{\text{hours}}$]

f. The student will study the decomposition reaction again at a constant temperature of 90°C, except this time, he will do so with two solutions in two different beakers: one with a pH of 7 and one with a pH of 1. The student will once again collect data on the concentration of urea over time with the same initial urea concentration and put his data in a table and graph it. The student will then compare the data of trial 2 (beaker w/ pH of 7) and trial 3 (beaker w/ pH of 13) to trial 1 (beaker w/ pH

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ADDITIONAL PAGE FOR ANSWERING QUESTION 2

Of [B] to see if [OH] impacts the rate of reaction. If he notices a change in the graph, then OH^- must impact the reaction rate.

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2. Answer the following questions about the isomers fulminic acid and isocyanic acid.

Two possible Lewis electron-dot diagrams for fulminic acid, HCNO, are shown below.

H—C≡N—Ö: H—C̈=N=Ö:

(a) Explain why the diagram on the left is the better representation for the bonding in fulminic acid. Justify your choice based on formal charges.

Fulminic acid can convert to isocyanic acid according to the equation below.

$$HCNO(g) \rightleftarrows HNCO(g)$$

fulminic acid   *isocyanic acid*

Fulminic Acid	Isocyanic Acid
H—C≡N—Ö:	H—N̈=C=Ö:

(b) Using the Lewis electron-dot diagrams of fulminic acid and isocyanic acid shown in the boxes above and the table of average bond enthalpies below, determine the value of $\Delta H°$ for the reaction of $HCNO(g)$ to form $HNCO(g)$.

Bond	Enthalpy (kJ/mol)	Bond	Enthalpy (kJ/mol)	Bond	Enthalpy (kJ/mol)
N–O	201	C=N	615	H–C	413
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(c) A student claims that $\Delta S°$ for the reaction is close to zero. Explain why the student's claim is accurate.

(d) Which species, fulminic acid (HCNO) or isocyanic acid (HNCO), is present in higher concentration at equilibrium at 298 K? Justify your answer in terms of thermodynamic favorability and the equilibrium constant.

The ammonium salt of isocyanic acid is a product of the decomposition of urea, $CO(NH_2)_2$, represented below.

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A student studying the decomposition reaction runs the reaction at 90°C. The student collects data on the concentration of urea as a function of time, as shown by the data table and the graph below.

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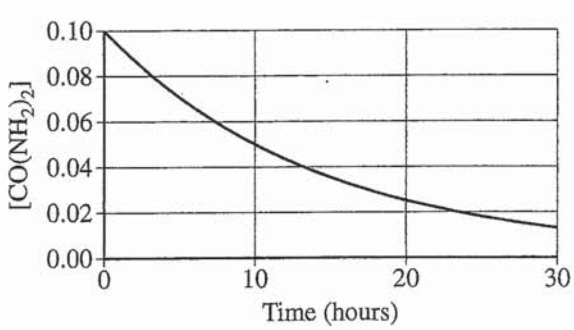

(e) The student proposes that the rate law is $rate = k[CO(NH_2)_2]$.

(i) Explain how the data support the student's proposed rate law.

(ii) Using the proposed rate law and the student's results, determine the value of the rate constant, k. Include units with your answer.

(f) The student learns that the decomposition reaction was run in a solution with a pH of 13. Briefly describe an experiment, including the initial conditions that you would change and the data you would gather, to determine whether the rate of the reaction depends on the concentration of $OH^-(aq)$.

a)

$^{(0)}H - C^{(0)} \equiv N^{(1+)} - \ddot{O}:^{(1-)}$ $\quad\quad$ $H^{(0)} - C^{(1-)} = N^{(1+)} = O^{(0)}$

The diagram on the left is a better representation for the bonding in Fulminic acid because the Carbon in the left diagram has a formal charge of 0 while the carbon in the right diagram has a formal charge of 1−. A formal charge of 0 is preferred.

b) Bonds broken − Bonds Formed = $\Delta H°$

H−C	413 kJ/mol	H−N	391 kJ/mol
C≡N	+ 891 kJ/mol	N=C	+ 615 kJ/mol
N−O	+ 201 kJ/mol	C=O	+ 745 kJ/mol

1505 kJ/mol − 1751 kJ/mol = **−246 kJ/mol**

C, The students claim is accurate because both the reactants and the products have one mol of gas. A phase change to gas or an increase in mols of gas would indicate an increase in entropy. Because there is no change of phase or mols it is likely that the $\Delta S°$ for the reaction is close to zero.

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d. isocyanic acid is present at a higher concentration at equilibrium at 298k because ΔG is negative and k is > 1

$\Delta G° = \Delta H° - T\Delta S°$ Assumption that ΔS° is 0 this favors the products (HNCO).

$\Delta G° = -246 \frac{kJ}{mol} - 298k(0)$

$\Delta G° = -246\ kJ/mol$ $\quad -246 \frac{kJ}{mol} \times \frac{1000 J}{1 kJ} = -246000 \frac{J}{mol}$

$\Delta G° = -RT\ln K$

$-246000 \frac{J}{mol} = 8.314 \frac{J}{mol\,K} (298k)(\ln k)$

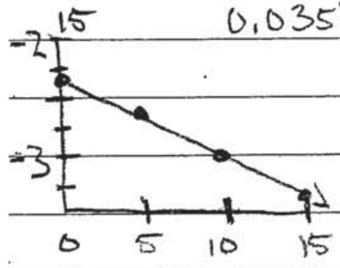
$99.3 = \ln k$

$e^{99.3} = K$

$K = 1.33 \times 10^{43}$

e. i.

Time	$[CO(NH_2)_2]$	$\ln[CO(NH_2)_2]$
0	0.1000 M	−2.302
5	0.0707 M	−2.65
10	0.0500 M	−3.00
15	0.0354 M	−3.34



The data supports the students rate law because when the $\ln[CO(NH_2)_2]$ is plotted V. Time (s) the resulting graph is a straight line with negative slope. This shows that the reaction is 1st order which supports the students rate law.

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e.
ii. $\ln[A]_t - \ln[A]_0 = -kt$ rate = $k[Co(NH_2)_2]$
$\ln[0.0500M] - \ln[.1000M] = -k(10)$ 1st order ↑
$k = 0.0693\ s^{-1}$

f. I would run the reaction in a multiple solutions with pH's ranging from 0-14 with the initial $[CO(NH_2)_2]$ the same then measure the $[OH^-]$ and $[CO(NH_2)_2]$ over time.

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(a) Explain why the diagram on the left is the better representation for the bonding in fulminic acid. Justify your choice based on formal charges.

Fulminic acid can convert to isocyanic acid according to the equation below.

$$HCNO(g) \rightleftarrows HNCO(g)$$

fulminic acid   *isocyanic acid*

Fulminic Acid	Isocyanic Acid
H—C≡N—Ö:	H—N̈=C=Ö:

(b) Using the Lewis electron-dot diagrams of fulminic acid and isocyanic acid shown in the boxes above and the table of average bond enthalpies below, determine the value of $\Delta H°$ for the reaction of $HCNO(g)$ to form $HNCO(g)$.

Bond	Enthalpy (kJ/mol)	Bond	Enthalpy (kJ/mol)	Bond	Enthalpy (kJ/mol)
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(c) A student claims that $\Delta S°$ for the reaction is close to zero. Explain why the student's claim is accurate.

(d) Which species, fulminic acid (HCNO) or isocyanic acid (HNCO), is present in higher concentration at equilibrium at 298 K? Justify your answer in terms of thermodynamic favorability and the equilibrium constant.

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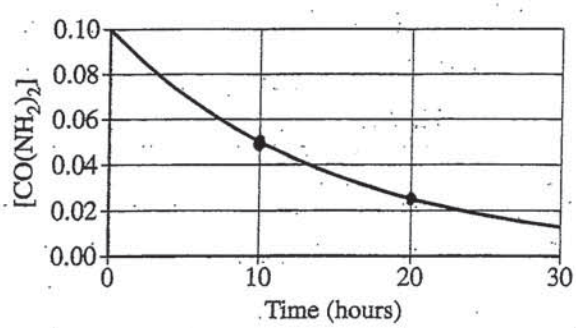

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(e) The student proposes that the rate law is $rate = k[CO(NH_2)_2]$.

(i) Explain how the data support the student's proposed rate law.

(ii) Using the proposed rate law and the student's results, determine the value of the rate constant, k. Include units with your answer.

(f) The student learns that the decomposition reaction was run in a solution with a pH of 13. Briefly describe an experiment, including the initial conditions that you would change and the data you would gather, to determine whether the rate of the reaction depends on the concentration of $OH^-(aq)$.

a- carbon usually forms 4 bonds with no unshared pairs. The diagram on the left shows this representation. This way, all the atoms are satisfied

b- (+413) (−391)
(+891) + (−615)
+ (+201) + (−745)
1505 − 1751 = −246 KJ/mol

c- The rxn is moving from 1 mol gas to 1 mol gas. This indicates that the freedom / disorder of the mlcls has not changed, so ΔS° would be close to 0

d- The rxn is exothermic due to −ΔH°, so it favors the forward direction. So the products, or HNCO will be present in higher concentration @ equil

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e- i) the graph indicates that the rate is directly proportional to the [$CO(NH_2)_2$]. Every 10 minutes that go by, the [$CO(NH_2)_2$] is 1/2 of what it was.

ii) $20 = k(.0250)$

$k = 8.00 \times 10^2$ hr/M

f- Keep the temp, pressure, and volume the same. change the concentration of OH^- and record data in table. Check to see if time changed as [OH^-] was increased/decreased

Question 2

Overview

In parts (a) through (f) this question assessed students' understanding of several fundamental concepts: formal charge, determination of $\Delta H°$ and $\Delta S°$ of a reaction, and the relationships between concentrations, thermodynamic favorability, and K. In parts (e) and (f) the questions focused on the evaluation of data for a first-order reaction: the decomposition of urea.

In this question the Learning Objectives (LO) assessed were 2.21, 4.1, 4.2, 4.3, 5.8, 5.12, and 5.13. The Science Practices (SP) assessed were 1.4, 2.2, 2.3, 4.2, 5.1, 6.4, 7.1, and 7.2.

In part (a) students were asked to explain why one resonance structure of fulminic acid was better using formal charges. In part (b) students were asked to determine ΔH°_{rxn} for the conversion of fulminic acid (HCNO) to isocyanic acid (HNCO) using the given bond enthalpies. In part (c) students were asked to explain why $\Delta S°$ would be close to zero for the conversion of HCNO(g) to HNCO(g). In part (d) using their answers to parts (b) and (c), students were asked to choose which species would be present in higher concentration at equilibrium and to justify their choice in terms of thermodynamic favorability and the equilibrium constant. In part (e)(i) using a data table and graph of $[CO(NH_2)_2]$ vs. time, students were asked to explain how the data supported a first-order rate law for the decomposition of urea. In part (e)(ii) using the proposed rate law and the data, students were asked to calculate the rate constant for the decomposition of urea. In part (f) given the information that the decomposition reaction was run at pH 13, students were asked to describe an experiment that would determine whether the reaction rate depended upon the concentration of OH^-.

Sample: 2A
Score: 10

This response earned 10 out of 10 possible points. The response earned 2 points in part (a) for the correct assignment of formal charges on the atoms in both diagrams and for correctly explaining that the structure on the left is better because the negative formal charge is better on the more electronegative oxygen. The response earned 1 point in part (b) for subtracting the enthalpies of bonds formed from the enthalpies of bonds broken and 1 point for the correct calculation of $\Delta H°$. The student earned 1 point in part (c) for indicating that the entropy change would be close to zero because there are the same number of moles of reactants and products and that there is no change of phase. The response earned 1 point in part (d) because the student correctly indicates that HNCO would be present in higher concentration and explains that because $\Delta H°$ is negative and $\Delta S°$ is close to zero, $\Delta G°$ would also be negative, making the reaction thermodynamically favorable. The response earned 1 additional point because the student indicates that when a reaction is thermodynamically favorable, $K > 1$. In part (e)(i) the student earned 1 point for correctly indicating that the reaction has a constant half-life of 10 hours, and a constant half-life is indicative of a first-order reaction. The response earned 1 point in part (e)(ii) for the correct calculation of k, with correct units. The response earned 1 point in part (f) for the description of an experiment in which solutions at a pH of 1 and 7 would be used, and the data would be collected and compared to determine whether $[OH^-]$ affected the rate.

Sample: 2B
Score: 8

This response earned 8 out of 10 possible points. In part (a) 1 point was earned for the correct assignment of formal charges on the atoms in both diagrams. The second point was not earned because the student indicates that the diagram on the left is better because C has a formal charge of zero, with no mention of the charge on oxygen in each diagram. The response earned 1 point in part (b) for subtracting the enthalpies of bonds formed from the enthalpies of bonds broken and 1 point for the correct calculation of $\Delta H°$. In part (c) 1 point was earned for the explanation that

Question 2 (continued)

the entropy change would be close to zero because there is no change in phase or number of molecules (moles). In part (d) 1 point was earned for correctly indicating that HNCO would be present in higher concentration and for correctly indicating that because $\Delta H°$ is negative and $\Delta S°$ is close to zero, $\Delta G°$ would also be negative, making the reaction thermodynamically favorable. The second point was earned for showing by calculation that $K > 1$ under the stated conditions. In part (e)(i) 1 point was earned for the graph of ln[$CO(NH_2)_2$] vs. time, which shows that the plot is a straight line and is indicative of a first-order reaction. No point was earned in part (e)(ii) because the units are incorrect. In part (f) 1 point was earned for the description of an experiment in which data would be collected at different pHs.

Sample: 2C
Score: 5

This response earned 5 out of 10 possible points. In part (a) the first point was not earned because there are no formal charges assigned in either diagram. The second point was not earned because the student incorrectly indicates that the diagram on the left is better because carbon has four bonds and no unshared pairs of electrons, and the student does not consider the other atoms in the molecule. The response earned 1 point in part (b) for subtracting the enthalpies of bonds formed from the enthalpies of bonds broken and 1 point for the correct calculation of $\Delta H°$. In part (c) 1 point was earned for the explanation that the entropy change would be close to zero because 1 mole of gas is converted into 1 mole of a different gas. No points were earned in part (d) because the student indicates that HNCO would be in greater concentration at equilibrium because the reaction is exothermic, with no mention of the role of entropy in determining thermodynamic favorability, and because there is no mention of K. In part (e)(i) 1 point was earned for the observation that the [$CO(NH_2)_2$] decreased by half at regular time intervals, which is consistent with a first-order rate law. The response earned no point in part (e)(ii). In part (f) 1 point was earned for the description of an experiment in which different OH^- concentrations would be used and the rates compared.