

AP® CHEMISTRY
2017 SCORING GUIDELINES

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.



- (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.

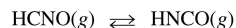
In the diagram on the left, the C atom has a formal charge of zero and the O atom has a formal charge of -1 . In the diagram on the right, the C atom has a formal charge of -1 and the O atom has a formal charge of zero.

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 assignment of formal charges in the two diagrams.

1 point is earned for a correct explanation.

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



fulminic acid *isocyanic acid*

Fulminic Acid			Isocyanic Acid		
$\text{H}-\text{C}\equiv\text{N}-\ddot{\text{O}}:$			$\text{H}-\ddot{\text{N}}=\text{C}=\ddot{\text{O}}:$		

- (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 ΔH° 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

$$\begin{aligned}\Delta H^\circ &= \Sigma(\text{enthalpies of bonds broken}) - \Sigma(\text{enthalpies of bonds formed}) \\ &= 1505 \text{ kJ/mol} - 1751 \text{ kJ/mol} \\ &= -246 \text{ kJ/mol}_{\text{rxn}}\end{aligned}$$

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 ΔH° .

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Question 2 (continued)

- (c) A student claims that ΔS° 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.

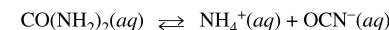
Isocyanic acid (HNCO) will be present in higher concentration.
 ΔG° is essentially equal to ΔH° because ΔS° is essentially zero, so $\Delta G^\circ \approx -246 \text{ kJ/mol}_{\text{rxn}}$, indicating the forward reaction is thermodynamically favorable.

Since ΔG° is negative, $K > 1$ ($\Delta G^\circ = -RT \ln K$), resulting in a higher concentration of product than reactant at equilibrium.

1 point is earned for the correct choice **with** a valid justification.
(Calculation of ΔG° is a sufficient justification.)

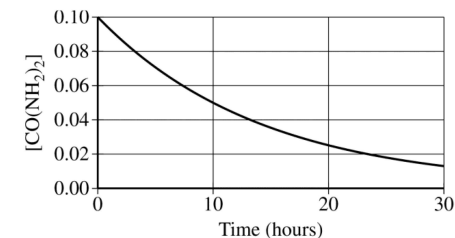
1 point is earned for correctly connecting thermodynamic favorability to the equilibrium constant, K .

The ammonium salt of isocyanic acid is a product of the decomposition of urea, $\text{CO}(\text{NH}_2)_2$, represented below.



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)	$[\text{CO}(\text{NH}_2)_2]$
0	0.1000
5	0.0707
10	0.0500
15	0.0354
20	0.0250
25	0.0177
30	0.0125



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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.