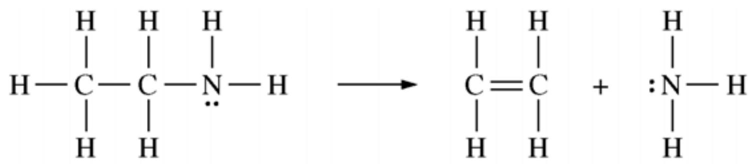
AP® CHEMISTRY
2012 SCORING GUIDELINES

Question 3
(9 points)



A sample of $CH_3CH_2NH_2$ is placed in an insulated container, where it decomposes into ethene and ammonia according to the reaction represented above.

Substance	Absolute Entropy, $S°$, in J/(mol·K) at 298 K
$CH_3CH_2NH_2(g)$	284.9
$CH_2CH_2(g)$	219.3
$NH_3(g)$	192.8

(a) Using the data in the table above, calculate the value, in $J/(mol_{rxn} \cdot K)$, of the standard entropy change, $\Delta S°$, for the reaction at 298 K.

$\Delta S^\circ_{rxn} = \Sigma S^\circ_{products} - \Sigma S^\circ_{reactants}$ $\Delta S^\circ_{rxn} = [(219.3 + 192.8) - 284.9]\ J/(mol_{rxn} \cdot K)$ $= 127.2\ J/(mol_{rxn} \cdot K)$	1 point is earned for the correct $\Delta S°$.

(b) Using the data in the table below, calculate the value, in kJ/mol_{rxn}, of the standard enthalpy change, $\Delta H°$, for the reaction at 298 K.

Bond	C–C	C = C	C–H	C–N	N–H
Average Bond Enthalpy (kJ/mol)	348	614	413	293	391

$\Delta H°$ = enthalpy of bonds broken – enthalpy of bonds formed $\Delta H° = [5(\Delta H_{C\text{-}H}) + (\Delta H_{C\text{-}N}) + (\Delta H_{C\text{-}C}) + 2(\Delta H_{N\text{-}H})] -$ $[4(\Delta H_{C\text{-}H}) + (\Delta H_{C=C}) + 3(\Delta H_{N\text{-}H})]$ $= [5(413) + 293 + 348 + 2(391)] - [4(413) + 614 + 3(391)] = 49\ kJ/mol_{rxn}$ **OR** $\Delta H° = [(\Delta H_{C\text{-}H}) + (\Delta H_{C\text{-}N}) + (\Delta H_{C\text{-}C})] - [(\Delta H_{C=C}) + (\Delta H_{N\text{-}H})]$ $= [413 + 293 + 348]\ kJ/mol - [614 + 391]\ kJ/mol = 49\ kJ/mol_{rxn}$	1 point is earned for the correct bond count and use of values from table. 1 point is earned for the correct setup in terms of bonds broken minus bonds formed and calculated $\Delta H°$.

Question 3 (continued)

(c) Based on your answer to part (b), predict whether the temperature of the contents of the insulated container will increase, decrease, or remain the same as the reaction proceeds. Justify your prediction.

The temperature of the contents should decrease because the reaction is endothermic, as indicated by the positive $\Delta H°$.	1 point is earned for the correct choice with explanation.

An experiment is carried out to measure the rate of the reaction, which is first order. A 4.70×10^{-3} mol sample of $CH_3CH_2NH_2$ is placed in a previously evacuated 2.00 L container at 773 K. After 20.0 minutes, the concentration of the $CH_3CH_2NH_2$ is found to be 3.60×10^{-4} mol/L.

(d) Calculate the rate constant for the reaction at 773 K. Include units with your answer.

$\ln[A]_t - \ln[A]_o = -kt$ $\ln(3.60 \times 10^{-4}\text{ mol/L}) - \ln\left(\frac{4.70 \times 10^{-3}\text{ mol}}{2.00\text{ L}}\right) = -k(20.0\text{ min})$ $-7.929 - (-6.053) = -k(20.0\text{ min})$ $k = 9.38 \times 10^{-2}\text{ min}^{-1}$	1 point is earned for the initial concentration of $CH_3CH_2NH_2$. 1 point is earned for the correct setup of the first order integrated rate law equation. 1 point is earned for the calculated result with unit.

(e) Calculate the initial rate, in M min^{-1}, of the reaction at 773 K.

initial rate $= k[CH_3CH_2NH_2] = (9.38 \times 10^{-2}\text{ min}^{-1})\left(\frac{4.70 \times 10^{-3}\text{ mol}}{2.00\text{ L}}\right)$ $= 2.20 \times 10^{-4}\ M\text{ min}^{-1}$	1 point is earned for the calculated result.

(f) If $\frac{1}{[CH_3CH_2NH_2]}$ is plotted versus time for this reaction, would the plot result in a straight line or would it result in a curve? Explain your reasoning.

The plot would produce a curve; had the reaction been second order the plot would have been a straight line. A plot of $\ln[CH_3CH_2NH_2]$ vs. t would have yielded a straight line.	1 point is earned for the correct choice with explanation.

3A

3. A sample of $CH_3CH_2NH_2$ is placed in an insulated container, where it decomposes into ethene and ammonia according to the reaction represented above.

Substance	Absolute Entropy, $S°$, in J/(mol·K) at 298 K
$CH_3CH_2NH_2(g)$	284.9
$CH_2CH_2(g)$	219.3
$NH_3(g)$	192.8

(a) Using the data in the table above, calculate the value, in J/(mol_{rxn}·K), of the standard entropy change, $\Delta S°$, for the reaction at 298 K.

(b) Using the data in the table below, calculate the value, in kJ/mol_{rxn}, of the standard enthalpy change, $\Delta H°$, for the reaction at 298 K.

Bond	C–C	C=C	C–H	C–N	N–H
Average Bond Enthalpy (kJ/mol)	348	614	413	293	391

(c) Based on your answer to part (b), predict whether the temperature of the contents of the insulated container will increase, decrease, or remain the same as the reaction proceeds. Justify your prediction.

An experiment is carried out to measure the rate of the reaction, which is first order. A 4.70×10^{-3} mol sample of $CH_3CH_2NH_2$ is placed in a previously evacuated 2.00 L container at 773 K. After 20.0 minutes, the concentration of the $CH_3CH_2NH_2$ is found to be 3.60×10^{-4} mol/L.

(d) Calculate the rate constant for the reaction at 773 K. Include units with your answer.

(e) Calculate the initial rate, in M min^{-1}, of the reaction at 773 K.

(f) If $\frac{1}{[CH_3CH_2NH_2]}$ is plotted versus time for this reaction, would the plot result in a straight line or would it result in a curve? Explain your reasoning.

a) $\Delta S° = \sum S°\ products - \sum S°\ reactants$

$= (219.3\ \frac{J}{mol\text{-}K} + 192.8\ \frac{J}{mol\text{-}K}) - (284.9\ \frac{J}{mol\text{-}K}) = 127.2\ \frac{J}{mol_{rxn}\cdot K}$

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b) bonds broken: 1 C-H, 1 C-C, 1 C-N

bonds formed: 1 C=C, 1 N-H

$\Delta H° = \Delta H_{\text{bonds broken}} - \Delta H_{\text{bonds formed}}$

$= (413 \frac{kJ}{mol} + 348 \frac{kJ}{mol} + 293 \frac{kJ}{mol}) - (614 \frac{kJ}{mol} + 391 \frac{kJ}{mol})$

$= 49$ kJ/mol$_{rxn}$

c) As the reaction proceeds, the temperature of the container should decrease because the $\Delta H°_{rxn}$ is positive, indicating the reaction is endothermic.

d) initial concentration of $CH_3CH_2NH_2 = \frac{4.70 \times 10^{-3} \text{ mol}}{2.00 \text{ L}} = 2.35 \times 10^{-3}$ M

$\ln[A]_t - \ln[A]_0 = -kt$

$\ln(3.60 \times 10^{-4} \text{ M}) - \ln(2.35 \times 10^{-3} \text{ M}) = -k(20.0 \text{ mins})$

$k = 0.0938 \text{ min}^{-1}$

e) initial rate $= k[CH_3CH_2NH_2] = (0.0938 \text{ min}^{-1})(2.35 \times 10^{-3} \text{ M})$

$= 2.20 \times 10^{-4}$ M·min^{-1}

f) It should result in a curve; since the reaction is first-order, the graph of $\ln[CH_3CH_2NH_2]$ vs. time is linear. The graph of $\frac{1}{[CH_3CH_2NH_2]}$ vs time would only be linear for a second-order reaction.

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ADDITIONAL PAGE FOR ANSWERING QUESTION 3

a.) $\Delta S° = \sum \Delta S°_{products} - \sum \Delta S°_{reactants}$

$\Delta S° = (219.3 + 192.8) - (284.9) = 127.2\ J/(mol_{rxn} \cdot K)$

b.) $\Delta H° = \sum \Delta H°_{f\ products} - \sum \Delta H°_{f\ reactants}$

$\sum \Delta H°_{f\ products} = 5(413) + 293 + (391)2 = 3140$

$\sum \Delta H°_{f\ reactants} = 614 + 4(413) + 3(391) = 3439$

$\Delta H° = 3140 - 3439 = -299\ kJ/mol_{rxn}$

c.) $\Delta G° = \Delta H° - T\Delta S°$

$\Delta G° = -299 - T(127.2)$

Temperature will decrease as the reaction proceeds, because in order for the reaction to proceed, $\Delta G°$, or the change in free energy needs to increase, and for that to happen, T will have to decrease.

d.) $\ln[A]_t - \ln[A]_0 = -kt$

$\ln(3.6E-4) - \ln(.00235) = -k(20)$ $k = .0938\ m^{-1}$

e.) $Rate = k[CH_3CH_2NH_2]$ $Rate_0 = .0938[CH_3CH_2NH_2]_0$

$Rate_0 = .0938(.00235) =$ ~~[illegible]~~ $= 2.20E-4\ M/min$

f.) This would create a curve, because in order for a plot of $\frac{1}{[CH_3CH_2NH_2]}$ versus time to be straight, it would have to be a second order reaction.

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3C

a) $\Delta S° = \sum \Delta S°$ products $- \sum \Delta S°$ reactants
$= [(219.3\ J/mol\,K) + (192.8\ J/mol\,K)] - [284.9\ J/mol\,K]$
$= 127.2\ J/mol\,K$

b) $\Delta H° = \sum \Delta H°$ products $- \sum \Delta H°$ reactants
$= [(3.391\ kJ/mol) + (4.413\ kJ/mol) + (1.614\ kJ/mol)] - [(1.348\ kJ/mol) + (5.413\ kJ/mol) + (2.391\ kJ/mol) + (1.293\ kJ/mol)]$
$= 3439\ kJ/mol - 3488\ kJ/mol$
$= -49\ kJ/mol$

c) it will decrease because the reaction is spontaneous, meaning it will move in the forward direction by itself. This means reactants will be used up and products will form, decreasing the amount of $CH_3CH_2NH_2(g)$

d) rate = k [C]   ($CH_3CH_2NH_2(g) = C$)
$[C] = \frac{.00434\ mol}{2\ L}$

[C] = [.00217] change in 20 minutes
$\frac{[.00217]}{20\ min} = k\ [.00235]$ ← initial $[C] = \frac{4.7 \times 10^{-3}\ mol}{2.0\ L}$

$k = .0462\ \frac{1}{min}$

e) rate = $.0462\ \frac{1}{min}\ [.00235]$
rate = $1.09 \times 10^{-4}\ \frac{M}{min}$

f) it would be a curve because it is a 1st order reaction. For 1st order reactions you have to plot ln [C] versus time to get a straight line. $\frac{1}{[C]}$ would be a straight line in a 2order reaction

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Question 3

Overview

This question assessed students' understanding of fundamental concepts of thermodynamics and kinetics. Part (a) presented students with standard entropy values for reactants and products and required them to calculate $\Delta S°$ for the reaction. In part (b) students were asked to calculate $\Delta H°$ for the reaction from a table of average bond enthalpies and structural formulas for all species. Part (c) required students to interpret the temperature change of an insulated container in which the reaction occurs. The focus of the question changed from thermodynamics to kinetics in parts (d) through (f). In part (d) students were presented with data from which to determine initial and final reactant concentrations and were told that the decomposition reaction is first order. Students were first required to determine the initial concentration of reactant and to apply the concentrations to the integrated rate law for first-order reactions to determine the value of the rate constant, k, with appropriate units. Students were then required to determine the initial reaction rate for the conditions given and, finally, to predict whether a graph of $1/[CH_3CH_2NH_2]$ versus time would be linear or curved and to explain their reasoning.

Sample: 3A
Score: 9

In part (a) 1 point was earned for correctly calculating the value of $\Delta S°$ for the reaction. In part (b) 2 points were earned for identifying the bonds broken and formed in the reaction and correctly determining $\Delta H°$. In part (c) 1 point was earned for stating the correct change in temperature and referring to the sign of $\Delta H°$. Part (d) earned 3 points: 1 point for correctly determining the initial concentration of $CH_3CH_2NH_2$, 1 point for correctly substituting the appropriate values into the integrated rate law for a first-order reaction, and 1 point for calculating a correct value of the rate constant with appropriate unit. Part (e) earned 1 point for calculating the correct initial reaction rate, and part (f) earned 1 point for stating that the graph of $1/[CH_3CH_2NH_2]$ yields a curve and giving a correct explanation.

Sample: 3B
Score: 7

In part (b) 1 of 2 points was earned. The student correctly subtracts bond enthalpies for the bonds that were formed from the bond enthalpies of the bonds that were broken in the reaction but does not account for the breaking of the C—C single bond in the reactant molecule. Part (c) did not earn a point because the temperature change is inconsistent with the sign of $\Delta H°$.

Sample: 3C
Score: 5

In part (b) 1 point was earned. The student correctly counts the total bonds in the reactant and product molecules; however, the student reverses the signs of the bond enthalpies. Part (c) did not earn a point because the temperature change is inconsistent with the sign of $\Delta H°$. Part (d) earned 1 point for determining the correct initial concentration of $CH_3CH_2NH_2$. Part (e) earned 1 point for calculating a rate consistent with the incorrect rate constant found in part (d).