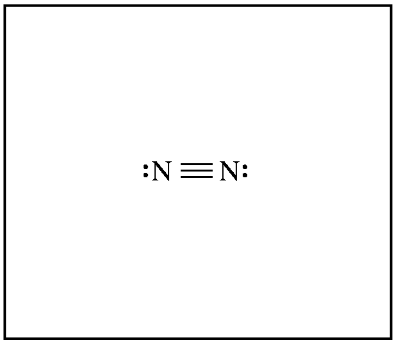
AP® CHEMISTRY
2009 SCORING GUIDELINES (Form B)

Question 5 (9 points)

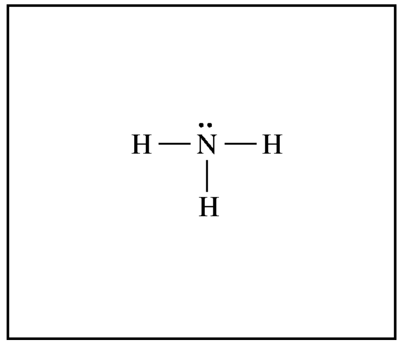
Answer the following questions about nitrogen, hydrogen, and ammonia.

(a) In the boxes below, draw the complete Lewis electron-dot diagrams for N_2 and NH_3.

N_2



NH_3



The correct structures are shown in the boxes above.	Two points are earned for the correct Lewis electron-dot diagrams (1 point each).

(b) Calculate the standard free-energy change, $\Delta G°$, that occurs when 12.0 g of $H_2(g)$ reacts with excess $N_2(g)$ at 298 K according to the reaction represented below.

$$N_2(g) + 3\,H_2(g) \rightleftarrows 2\,NH_3(g) \qquad \Delta G^{\circ}_{298} = -34 \text{ kJ mol}^{-1}$$

$12.0 \text{ g } H_2 \times \frac{1 \text{ mol } H_2}{2.0 \text{ g } H_2} \times \frac{1 \text{ mol reaction}}{3 \text{ mol } H_2} \times \frac{-34 \text{ kJ}}{1 \text{ mol reaction}} = \mathbf{-68 \text{ kJ}}$	One point is earned for the correct stoichiometry. One point is earned for the correct answer.

(c) Given that ΔH°_{298} for the reaction is $-92.2 \text{ kJ mol}^{-1}$, which is larger, the total bond dissociation energy of the reactants or the total bond dissociation energy of the products? Explain.

$\Delta H^{\circ}_{298} = \Sigma$ (bond energy of the reactants) $- \Sigma$ (bond energy of the products) Based on the equation above, for ΔH°_{298} to be negative, the total bond energy of the products must be larger than the total bond energy of the reactants. **OR** More energy is released as product bonds are formed than is absorbed as reactant bonds are broken.	One point is earned for the correct answer with the correct equation and explanation.

Question 5 (continued)

(d) The value of the standard entropy change, ΔS°_{298}, for the reaction is -199 J $mol^{-1}K^{-1}$. Explain why the value of ΔS°_{298} is negative.

All of the reactants and products in the reaction are in the gas phase, so the sign of the entropy change will depend on the number of moles of particles in the reactants and products. There are more moles of reactants (four) compared with moles of products (two), so there is a greater number of microstates in the reactants than in the products. Therefore the entropy decreases as the reaction proceeds (fewer possible microstates), and the sign of the entropy change is negative.	One point is earned for the correct explanation.

(e) Assume that ΔH° and ΔS° for the reaction are independent of temperature.

(i) Explain why there is a temperature above 298 K at which the algebraic sign of the value of ΔG° changes.

$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ As the temperature increases $\lvert T\Delta S^\circ \rvert$ will at some point exceed $\lvert \Delta H^\circ \rvert$. Because both ΔH° and ΔS° are negative, the sign of ΔG° will then change from negative to positive.	One point is earned for the correct explanation.

(ii) Theoretically, the best yields of ammonia should be achieved at low temperatures and high pressures. Explain.

<u>Low temperatures:</u> The reaction is exothermic. By Le Chatelier's principle, decreasing the temperature drives the reaction to the right to produce more heat energy, and thus more ammonia is produced.	One point is earned for explaining increased yield at low temperatures.
<u>High pressures:</u> For this reaction, higher pressure is achieved by decreasing the volume of the container. As pressure increases, the reaction equilibrium shifts in the direction that reduces the total number of particles (by Le Chatelier's principle). In this case, the product has fewer moles of particles than the reactants; thus product would be favored. Higher pressure therefore results in an increase in the amount of ammonia.	One point is earned for explaining increased yield at high pressures.

5A1

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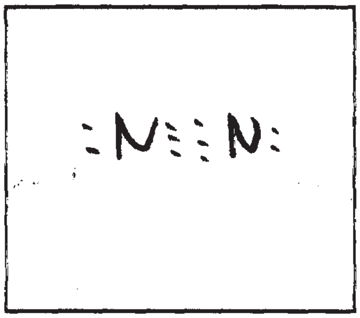
Answer Question 5 and Question 6. The Section II score weighting for these questions is 15 percent each.

Your responses to these questions will be graded on the basis of the accuracy and relevance of the information cited. Explanations should be clear and well organized. Examples and equations may be included in your responses where appropriate. Specific answers are preferable to broad, diffuse responses.

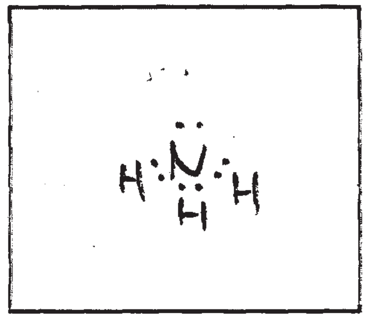
5. Answer the following questions about nitrogen, hydrogen, and ammonia.

   (a) In the boxes below, draw the complete Lewis electron-dot diagrams for N_2 and NH_3.

N_2



NH_3



   (b) Calculate the standard free-energy change, $\Delta G°$, that occurs when 12.0 g of $H_2(g)$ reacts with excess $N_2(g)$ at 298 K according to the reaction represented below.

$$N_2(g) + 3\,H_2(g) \rightleftarrows 2\,NH_3(g) \qquad \Delta G^\circ_{298} = -34 \text{ kJ mol}^{-1}$$

   (c) Given that ΔH°_{298} for the reaction is -92.2 kJ mol^{-1}, which is larger, the total bond dissociation energy of the reactants or the total bond dissociation energy of the products? Explain.

   (d) The value of the standard entropy change, ΔS°_{298}, for the reaction is -199 J mol^{-1}K^{-1}. Explain why the value of ΔS°_{298} is negative.

   (e) Assume that $\Delta H°$ and $\Delta S°$ for the reaction are independent of temperature.

      (i) Explain why there is a temperature above 298 K at which the algebraic sign of the value of $\Delta G°$ changes.

      (ii) Theoretically, the best yields of ammonia should be achieved at low temperatures and high pressures. Explain.

ADDITIONAL PAGE FOR ANSWERING QUESTION 5

(b) 12.0g of H_2 is approximately equal to 6mols.
Therefore 6/3 = 2 mols of nitrogen will react, since the hydrogen is the limiting reactant.
Therefore $\Delta G = -34 \times 2 = -68kJ$.

(c) ΔH of any reaction is equal to ΔH of the reaction where you dissociate all the reactant's bonds, and put them all back together to make the product. This is true by the Hess's Law, which suggests that ΔH is same as long as the reactants and the products are same between the 2 reactions. → Path does not matter

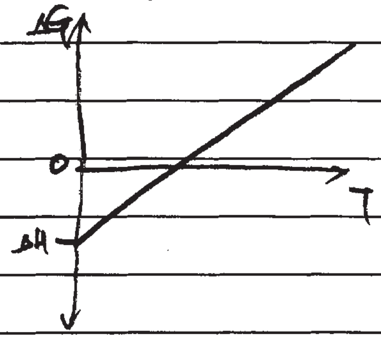
Therefore, $\Delta H = \Delta H$(Dissociating all reactant's bonds) + ΔH(Putting together)
= {Σ(Reactant's total bond dissociation energy) − Σ(Product's ″)}

Since ΔH(bond formation) = − ΔH(bond dissociation)

So since $\Delta H < 0$, Σ(Reactant) < Σ(Product)

(d) The entropy is the scale of randomness, and therefore will be proportional to the amount of gas, because more the gases are, more random it can get, mathematically.

(e)(i) Let's plot a graph of ΔG and T.



Since $\Delta G = \Delta H - T\Delta S$
$= (-\Delta S) \times T + \Delta H$,
the graph's slope would be $-\Delta S$ and the intersection with the y axis would be $(0, \Delta H)$

the graph is plotted like above since $\Delta H < 0$ and $\Delta S < 0$.
The intersection with the x-axis is calculated as so:
since $\Delta G = 0$, $\Delta H - T\Delta S = 0$ $\therefore T = \frac{\Delta H}{\Delta S}$
In this case it is $\frac{92200}{199} \doteqdot 461\,K$.
Therefore if the temperature is higher than 461K the ΔG is positive

(ii) Le Chatelier's Principle suggests that when an environmental change is done on a system with an equilibrium, the equilibrium will shift to reduce the change. Therefore if we lower the temperature, the system would try to raise it by exothermic reaction, which in this case is making ammonia. Also when we increase the pressure, the system would try to decrease it by reducing the moles of the gas, since in an ideal gas $P \propto n$. This is also done by making ammonia.

5B1

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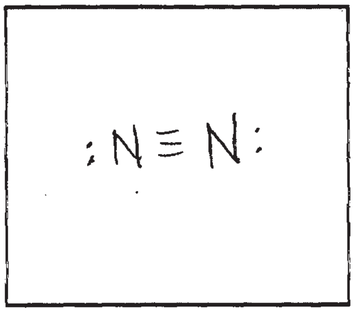
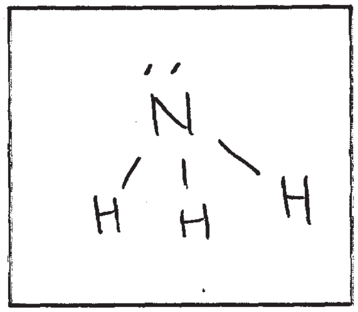


NH_3



(b) Calculate the standard free-energy change, $\Delta G°$, that occurs when 12.0 g of $H_2(g)$ reacts with excess $N_2(g)$ at 298 K according to the reaction represented below.

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(c) Given that $\Delta H°_{298}$ for the reaction is -92.2 kJ mol^{-1}, which is larger, the total bond dissociation energy of the reactants or the total bond dissociation energy of the products? Explain.

(d) The value of the standard entropy change, $\Delta S°_{298}$, for the reaction is -199 J $\text{mol}^{-1}\text{K}^{-1}$. Explain why the value of $\Delta S°_{298}$ is negative.

(e) Assume that $\Delta H°$ and $\Delta S°$ for the reaction are independent of temperature.

(i) Explain why there is a temperature above 298 K at which the algebraic sign of the value of $\Delta G°$ changes.

(ii) Theoretically, the best yields of ammonia should be achieved at low temperatures and high pressures. Explain.

b) $\Delta G° = 12.0\,g \cdot \frac{1 \text{ mol } H_2}{2.02\,g} \cdot \frac{2NH_3}{3H_2} \cdot \frac{-34\text{ kJ}}{\text{mol}}$

$\boxed{\Delta G° = -136 \text{ kJ}}$

c) The total bond dissociation energy of the products is larger. When $\Delta H° < 0$, the reaction is exothermic, so bonds

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are formed. $\Delta H^\circ = \Sigma$ bond energy of reactants $- \Sigma$ bond energy of products
Thus, since $\Delta H^\circ < 0$, the total bond dissociation energy of the products is greater.

d) ΔS°_{298} is negative. There are 4 moles of gas reactants and 2 moles of gas products. Therefore, the products are more orderly, causing a decrease in entropy, which explains why $\Delta S^\circ_{298} < 0$

e) (i) $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$. Since ΔH° and ΔS° are both negative,
$\Delta G^\circ = - - T(-)$
Therefore, at high temperatures, the value of $(-T\Delta S^\circ)$ will be more positive, which causes ΔG° to be positive.

(ii) At low temperatures, $\Delta G^\circ < 0$, so the reaction is spontaneous. At high pressures, the N_2 and NH_3 molecules have a greater tendency to collide and form NH_3.

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5G

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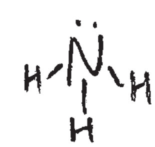
:N ≡ N:

NH_3



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(c) Given that ΔH°_{298} for the reaction is -92.2 kJ mol^{-1}, which is larger, the total bond dissociation energy of the reactants or the total bond dissociation energy of the products? Explain.

(d) The value of the standard entropy change, ΔS°_{298}, for the reaction is -199 J $\text{mol}^{-1}\text{K}^{-1}$. Explain why the value of ΔS°_{298} is negative.

(e) Assume that $\Delta H°$ and $\Delta S°$ for the reaction are independent of temperature.

(i) Explain why there is a temperature above 298 K at which the algebraic sign of the value of $\Delta G°$ changes.

(ii) Theoretically, the best yields of ammonia should be achieved at low temperatures and high pressures. Explain.

(b) NH_3 ⇒ 17g/mol 12g: $\frac{12}{17}$ mol

$\Delta G^\circ_{298} \times \frac{12}{17} = -24kJ$

(c) $\Delta H^\circ_{298} = \Sigma E_{\text{bond before}} - \Sigma E_{\text{bond after}} = -92.2kJ/mol$

∴, Bond dissociation energe of reactants is larger than products' energe.

 5C₂

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(d) Because the coefficeint of equation is decrease when ~~this~~ react, value of ΔS°_{rxn} is negative.

(e) (i) Because $\Delta G = \Delta H - T\Delta S$, ΔG changes because of change of temperature.

(ii) $\Delta G = \Delta H - T\Delta S$
To make ΔG negative, T sould be low because ΔS is negative.
And high pressures make react low ΔS.
Because ΔS is negative, high pressures makes react make more NH_3

 GO ON TO THE NEXT PAGE.

Question 5

Sample: 5A
Score: 9

This response earned all 9 points: 2 for part (a), 2 for part (b), 1 for part (c), 1 for part (d), 1 for part (e)(i), and 2 for part (e)(ii). In part (d) the point was earned for relating the negative change in entropy, associated with randomness, to the change in the number of moles of gas in the reaction.

Sample: 5B
Score: 6

This response earned 6 of the possible 9 points. In part (a) both points were earned for acceptable Lewis electron-dot diagrams of nitrogen gas and ammonia. In part (b) 1 point was earned for the application of an appropriate mass-to-mole conversion followed by the application of a ratio of moles to energy. Because the calculation includes an inappropriate conversion of moles of hydrogen to ammonia for the mole-to-energy conversion that follows, the response did not earn the second point. In part (c) 1 point was earned for a correct answer and explanation. In part (d) 1 point was earned for a correct answer with explanation. In part (e)(i) 1 point was earned for a correct explanation. In part (e)(ii) an incorrect explanation did not earn either of the possible points.

Sample: 5C
Score: 2

This response earned 2 of the possible 9 points. In part (a) both points were earned for acceptable Lewis electron-dot diagrams of nitrogen gas and ammonia. In part (b) the incorrect use of a mass-to-mass ratio with no mole-to-energy ratio did not earn either point. In part (c) the response presents a correct equation but interprets it incorrectly and thus did not earn the point. In part (d) there is reference to a decrease in the number of moles, but no mention of gas, randomness, or entropy; consequently no point was earned. In part (e)(i) presentation of the Gibb–Helmholtz equation, with an inadequate explanation, did not earn a point. In part (e)(ii) the response refers incorrectly to free energy, and while it mentions increased pressures favoring low entropy, it does not relate this to decreased gas pressure; hence, neither point was earned.