Essay Questions

1991

a) two points
$\Delta S$ will be negative. The system becomes more ordered as two gases form a solid.

b) two points
$\Delta H$ must be negative. For the reaction to be spontaneous, $\Delta G$ must be negative, so $\Delta H$ must be more negative than $-T\Delta S$ is positive.

c) two points
As $T$ increases, $-T\Delta S$ increases. Since $\Delta S$ is negative, the positive $-T\Delta S$ term will eventually exceed $\Delta H$ (which is negative), making $\Delta G$ positive. (In the absence of this, $\Delta G = \Delta H - T\Delta S$ and general discussion of the effect of $T$ and $\Delta S$ gets 1 point.)

d) two points
The equilibrium constant is 1. The system is at equilibrium at this temperature with an equal tendency to go in either direction.
OR
$\Delta G = 0$ at equilibrium so $K = 1$ in $\Delta G = -RT \ln K$
(In the absence of these, $\Delta G = -RT \ln K$ gets 1 point).
The above concludes the AP scoring standards published in 1991. The following is simply alternate ways of answering which the AP readers may or may not have given full credit to.

a) The amount of entropy goes down, $\Delta S$ is negative.
b) $\Delta G = \Delta H - T\Delta S$. If $\Delta S$ is negative, then $\Delta H$ must also be negative to get a negative $\Delta G$.
c) Let us say $\Delta G$ is positive when $\Delta H$ is positive and $\Delta S$ is positive. As $T$ goes up - $T\Delta S$ becomes more negative until it makes $\Delta G$ (which equals $\Delta H - T\Delta S$) become negative.
d) At the temperature when the direction changes, the rate forward = the rate reverse. Since $K = kf / kr$, this equals 1.

(1) AP® is a registered trademark of the College Board. The College Board was not involved in the production of and does not endorse this product. (2) Test Questions are Copyright © 1970-2008 by College Entrance Examination Board, Princeton, NJ. All rights reserved. For face-to-face teaching purposes, classroom teachers are permitted to reproduce the questions. Web or Mass distribution prohibited.
8 (a) $\Delta S < 0$  (1 point)
   The number of moles of gaseous products is less than the number of moles of gaseous reactants or a liquid is formed from gaseous reactants.

(b) $\Delta G < 0$  (1 point)
   $\Delta G$ becomes less negative as the temperature is increased since $\Delta S < 0$ and $\Delta G = \Delta H - T \Delta S$. (1 point)
   The term $-T \Delta S$ adds a positive number to $\Delta H$.

(c) $\Delta H < 0$  (1 point)
   The bond energy of the reactants is less than the bond energy of the products.

(d) The reaction has a high activation energy (1 point)
   It is kinetically slow, or a specific mention of the need for a catalyst or spark.
1994

**Question 6**

(a) Statement that $\Delta S^0$ is negative

3 moles of gas $\rightarrow$ 2 moles of gas plus solid,
(3 moles $\rightarrow$ 2 moles earns no points)
OR,

2 gases $\rightarrow$ 1 gas + solid,
OR,

use of $\Delta G^0 = \Delta H^0 - T\Delta S^0$ with $\Delta G^0 \rightarrow 0$

Note: If statement is that $\Delta S^0$ is positive, then explanation of
3 moles gas $\rightarrow$ 5 moles of gas earns 1 point
(3 moles $\rightarrow$ 5 moles earns no points)
If correct explanation for $\Delta S^0$ being negative is given
but wrong sign is stated, 1 point is earned.

(b) $\Delta G^0$ is less negative, goes to 0, goes +, gets larger

Explanation using $\Delta G^0 = \Delta H^0 - T\Delta S^0$

Note: if answer to (a) is that $\Delta S^0$ is positive, then full
credit can be earned here for correct reasoning based
on that assumption. An explanation that uses
Le Châtelier's principle based on sign of $\Delta H^0$ is NOT
valid here since system not at equilibrium.

(c) $K_{eq}$ decreases (exponent $\rightarrow$ more negative) as $T$ increases

OR,

$K_{eq}$ goes from $> 1$, to 1, to $< 1$, as $T$ increases

Correct explanation using the equation
$\Delta G^0 = -RT \ln K_{eq}$ (or $\ln(K_1/K_2) = \Delta H^0/R(1/T_2 - 1/T_1)$

OR,

higher $T$ favors the reverse reaction (Le Châtelier)
because the forward reaction is exothermic

Note: if answer for (a) is that $\Delta S^0$ is positive then statement
that $K_{eq}$ will decrease or increase depending on the relative
magnitude of $T$ and $\Delta S^0$ change earns 2 points. Recognition that
BOTH $\Delta G^0$ and $T$ are changing in $\Delta G^0 = -RT \ln K_{eq}$ is necessary.
Or, ignoring part (a), use of $\Delta H^0 < 0$ explanation to correctly
predict that $K_{eq}$ will decrease earns 2 points.

(d) Since $\Delta G^0 = 0$ at this point, the equation is $T = \Delta H^0/\Delta S^0$
($\Delta G^0 = \Delta H^0 - T\Delta S^0$ is NOT sufficient without $\Delta G^0 = 0$.)

Prediction is not exact because $\Delta H^0$ and/or $\Delta S^0$ vary with $T$

**General Note:** For parts (a), (b), and (c), just writing an equation is not
sufficient for the "explanation" point. To earn credit, the
student must connect the equation to issue to be explained.
QUESTION 2
(9 pts.)

a) \[ C_2H_8 + 5 O_2 \rightarrow 3 CO_2 + 4 H_2O \] (1 pt.)

Notes: ignore phases (even when wrong)
multiples are OK
if balanced wrong, parts b and c should be consistent

b) \[ 10.0 \text{ g} \ C_2H_8 \times \frac{1 \text{ mol} \ C_2H_8}{44.1 \text{ g} \ C_2H_8} = 0.227 \text{ mol} \ C_2H_8 \] (1 pt.)

\[ 0.227 \text{ mol} \ C_2H_8 \times \frac{5 \text{ mol} \ O_2}{1 \text{ mol} \ C_2H_8} = 1.13 \text{ mol} \ O_2 \] (1 pt.)

\[ V = \frac{(1.13 \text{ mol} \ O_2)(0.0821 \text{ L- atm/mol}^{\cdot} \text{K}^{\cdot})(303 \text{ K})}{1.00 \text{ atm}} = 28.1 \text{ L} \ O_2 \] (1 pt.)

\[ 28.1 \text{ L} \ O_2 \times \frac{100 \text{ L} \text{ air}}{21.0 \text{ L} \ O_2} = 134 \text{ L} \text{ air} \] (1 pt.)

Note: answer must be consistent with part a

c) \[ \Delta H_{\text{rxn}}^o = \sum \Delta H_f^o \text{ (products)} - \sum \Delta H_f^o \text{ (reactants)} \]

\[ -2,220.1 \text{ kJ} = [4(-285.3 \text{ kJ}) + 3(-393.5 \text{ kJ})] - [5(0 \text{ kJ}) + \Delta H_f^o \text{ (C}_2\text{H}_8)] \] (1 pt.)

\[ -2,220.1 \text{ kJ} = -1,141.2 \text{ kJ} - 1,180.5 \text{ kJ} - \Delta H_f^o \text{ (C}_2\text{H}_8) \]

\[ -2,220.1 \text{ kJ} = -2,321.7 \text{ kJ} - \Delta H_f^o \text{ (C}_2\text{H}_8) \]

\[ -101.6 \text{ kJ} = \Delta H_f^o \text{ (C}_2\text{H}_8) \] (1 pt.)

Notes: answer should be consistent with part a
1 point deducted if negative sign missing from answer
1 point deducted if \(-2,220.1 \text{ kJ} \) substituted for \(\Delta H_f^o \text{ (C}_2\text{H}_8)\)
no points earned if coefficients are inconsistent and not set equal to \(\Delta H_f^o\)

d) \[ 30.0 \text{ g} \ C_2H_8 \times \frac{1 \text{ mol} \ C_2H_8}{44.1 \text{ g} \ C_2H_8} \times \frac{2,220.1 \text{ kJ}}{1 \text{ mol} \ C_2H_8} = 1.51 \times 10^3 \text{ kJ} \] (1 pt.)

\[ 1.51 \times 10^3 \text{ kJ} = 1.51 \times 10^6 \text{ J} = (8,000 \text{ g})(4.18 \text{ J} \cdot \text{g}^{\cdot} \text{K}^{\cdot})(\Delta T) \]

\[ 45.1 \text{ K (or °C)} = \Delta T \] (1 pt.)

Notes: must correctly substitute into \(q = mc\Delta T\) for 1 point
1 point earned if \(q\) value wrong but \(\Delta T\) consistent
Question 7
(8 points)

(a) \( \Delta S^\circ \) is positive (or " + ", or " > 0 ")
Moles products > moles reactants

Note: all species are gaseous, so \( (g) \) need not be indicated. To earn credit, number of particles (moles) must be discussed. No explanation point earned for just noting that disorder increases, or that PCl\(_5\) is decomposing or dissociating.

(b) \( \Delta G^\circ \) will decrease (or become more negative, or become smaller).
\[
\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ,
\]
and since \( \Delta S^\circ \) is positive, \( T \Delta S^\circ \) is positive ( \( > 0 \)). Thus increasing \( T \) will result in a larger term being subtracted from \( \Delta H^\circ \), or
\[
\Delta G^\circ = -RT \ln K \quad \text{and} \quad K \uparrow \quad (\text{since} \quad T \uparrow).
\]

Note: Full credit earned for part (b) if:
\( \Delta S^\circ < 0 \) in part (a) \( \Rightarrow \) \( \Delta G^\circ \) is increasing because \( T \Delta S^\circ \) is added to \( \Delta H^\circ \), or,
\( \Delta S^\circ = 0 \) in part (a) \( \Rightarrow \) no change in \( \Delta G^\circ \)

(c) No change

\( p_{\text{He}} \) is not part of the:
\[
\begin{align*}
\text{reaction (He is not involved)} & \\
\text{law of mass action} & \\
\text{reaction quotient} & \\
\text{equilibrium constant expression}
\end{align*}
\]

hence altering \( p_{\text{He}} \) has no effect on the position at equilibrium.

(d) Moles of Cl\(_2\) will decrease

The decrease in volume leads to an increase in pressure (concentration), therefore the reaction shifts to the left because:
\[
Q > K_p \quad (Q > K_c), \text{ or,}
\]
the rate of the reverse reaction increases more than the rate of the forward reaction, or

Note: "Le Châtelier’s principle" alone is not sufficient to earn explanation point. If response suggests that the number of moles of Cl\(_2\) is halved because the system is "cut" in half, only 1 point is earned.
AP® CHEMISTRY
1999 SCORING GUIDELINES

Question 6

(a) (i) \(\Delta S^o\) is negative (-) OR \(\Delta S^o < 0\) OR entropy is decreasing. 1 pt

3 moles of gaseous particles are converted to 2 moles of solid/liquid. 1 pt

- One point earned for correct identification of (-) sign of \(\Delta S^o\)
- One point earned for correct explanation (mention of phases is crucial for point)
- No point earned if incorrect \(\Delta S^o\) sign is obtained from the presumed value of \(\Delta G^o\)

(ii) \(\Delta H^o\) drives the reaction. 1 pt

The decrease in entropy (\(\Delta S^o < 0\)) cannot drive the reaction, so the decrease in enthalpy (\(\Delta H^o < 0\)) MUST drive the reaction.

OR 1 pt

\(\Delta G^o = \Delta H^o - T\Delta S^o\); for a spontaneous reaction \(\Delta G^o < 0\), and a negative value of \(\Delta S^o\) causes a positive \(\Delta G^o\).

- One point earned for identifying \(\Delta H^o\) as the principal driving force for the reaction
- One point earned for correct justification
- Justification point earned by mentioning the effects of changes in entropy and enthalpy on the spontaneity of the reaction OR by a mathematical argument using the Gibbs-Helmholtz equation and some implication about the comparison between the effects of \(\Delta S^o\) and \(\Delta H^o\)

(iii) Given that \(\Delta G^o = \Delta H^o - T\Delta S^o\) and \(\Delta S^o < 0\), an increase in temperature causes an increase in the value of \(\Delta G^o\) (\(\Delta G^o\) becomes less negative). 1 pt

- One point earned for the description of the effect of an increase in temperature on \(\Delta S^o\) and consequently on \(\Delta G^o\)
- No point earned for an argument based on Le Châtelier’s principle

(b) (i) The reaction rate depends on the reaction kinetics, which is determined by the value of the activation energy, \(E_{act}\). If the activation energy is large, a reaction that is thermodynamically spontaneous may proceed very slowly (if at all). 1 pt

- One point earned for linking the rate of the reaction to the activation energy, which may be explained verbally or shown on a reaction profile diagram

(ii) The catalyst has no effect on the value of \(\Delta G^o\). 1 pt

The catalyst reduces the value of \(E_{act}\), increasing the rate of reaction, but has no effect on the values of \(\Delta H^o\) and \(\Delta S^o\), so it cannot affect the thermodynamics of the reaction. 1 pt

- One point earned for indicating no change in the value of \(\Delta G^o\)
- One point earned for indicating (verbally, or with a reaction-profile diagram) that the catalyst affects the activation energy

Copyright © 2001 by College Entrance Examination Board. All rights reserved. College Board, Advanced Placement Program, AP, and the acorn logo are registered trademarks of the College Entrance Examination Board.
**Question 6**
(10 points)

(a) \( \Delta H^o = 33 - (90. + 143) \) kJ = \(-200\) kJ
- Correct set up (work), a numerical result, and a “−” sign, earn this point
- No “math error” point deducted for computational mistakes

(b) \( \Delta S^o \) for this reaction should be small or negligible (near zero or zero)
- No point earned for statements that \( \Delta S^o \) is constant or the same

because

the number of moles (of gas) is the same on each side of the equation.
- Point may be earned even if first point not earned

(c) \( \Delta G^o \) is negative (−) at 298 K
- Point earned only if consistent with answers given in parts (a) and (b)

because

\( \Delta G^o = \Delta H^o - T(\Delta S^o) \), \( \Delta H^o \) is negative, and \( \Delta S^o \) is near zero, thus it follows that \( \Delta G^o \) will be negative.
- Equation need not be written explicitly to earn point

*Notes:* Responses that \( \Delta G^o \) is positive (+), or not able to be determined, are accepted together with appropriate explanations IF they are fully consistent with incorrect responses given in part (a) and/or part (b). Since question concerns the reaction at 298 K, discussion of what might happen at high or low temperatures does not earn any explanation point.

(d) When \([O_3]\) is held constant and \([NO]\) is doubled (as in Experiments 1 and 2),
the rate also doubles \( \Rightarrow \) reaction is first-order in \([NO]\).

When \([NO]\) is held constant and \([O_3]\) is doubled (as in Experiments 1 and 3),
the rate also doubles \( \Rightarrow \) reaction is first-order in \([O_3]\).

\[ \text{Rate} = k [O_3] [NO] \] (or \( \text{Rate} = k [O_3]^1[NO]^1 \), or \( \text{Rate} = 10^6 (x) [O_3] [NO] \))

*Notes:* First point for correctly determining the order with respect to \([NO]\) and work shown, second point earned for correctly determining the order with respect to \([O_3]\) and work shown, and third point earned for correctly writing a rate-law expression that is consistent with answers to analysis of experimental results.
Question 6
(continued)

Step 1 must be rate-determining, as the rate law for this elementary step is the only one that agrees with the rate law determined experimentally in part (d) above.

The following arguments are acceptable, but not required:
If Step 2 were the rate-determining step, then the reaction would be second-order with respect to \([O_3]\) – this is inconsistent with the kinetic data.
If Step 3 were the rate-determining step, then the reaction would be second-order with respect to \([NO]\) – this is inconsistent with the kinetic data.

Notes: Two points are earned for identifying Step 1 as the rate-determining step and giving a valid explanation relating the similarity of the rate law of the slow step to that found from the experimental results. Only one point is earned for identifying Step 1 as the rate-determining step but only a minimal or partly incorrect explanation is given (e.g., an explanation based solely on the fact that both reactant molecules are only present in Step 1). Two points may be earned for identifying Step 2 or Step 3 as the rate-determining step IF the rate law determined in part (d) contains \([O_3]^2\) or \([NO]^2\), respectively.
7. Answer the following questions that relate to the chemistry of nitrogen.

(a) Two nitrogen atoms combine to form a nitrogen molecule, as represented by the following equation.

\[ 2 \text{N}(g) \rightarrow \text{N}_2(g) \]

Using the table of average bond energies below, determine the enthalpy change, \(\Delta H\), for the reaction.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Average Bond Energy (kJ mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>N = N</td>
<td>160</td>
</tr>
<tr>
<td>N = N</td>
<td>420</td>
</tr>
<tr>
<td>N = N</td>
<td>950</td>
</tr>
</tbody>
</table>

\[ \Delta H = -950 \text{ kJ} \]

The reaction is exothermic because the chemical equation shows the formation of the N = N bond.

1 point for correct sign
1 point for magnitude

(b) The reaction between nitrogen and hydrogen to form ammonia is represented below.

\[ \text{N}_2(g) + 3 \text{H}_2(g) \rightarrow 2 \text{NH}_3(g) \quad \Delta H^\circ = -92.2 \text{ kJ} \]

Predict the sign of the standard entropy change, \(\Delta S^\circ\), for the reaction. Justify your answer.

\(\Delta S^\circ\) is negative. There are fewer moles of product gas (2 mol) compared to reactant gases (4 mol), so the reaction is becoming more ordered.

1 point for correct sign
1 point for indicating fewer moles of products compared to reactants (in the gas phase)

(c) The value of \(\Delta G^\circ\) for the reaction represented in part (b) is negative at low temperatures but positive at high temperatures. Explain.

\[ \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \]

\(\Delta H^\circ\) and \(\Delta S^\circ\) are negative. At low temperatures, the \(T\Delta S^\circ\) term is smaller than \(\Delta H^\circ\), and \(\Delta G^\circ\) is negative. At high temperatures, the \(T\Delta S^\circ\) term is higher than \(\Delta H^\circ\), and \(\Delta G^\circ\) is positive.

1 point each for using \(\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ\) to explain the sign of \(\Delta G^\circ\) at high and low temperatures.
(d) When \( \text{N}_2(g) \) and \( \text{H}_2(g) \) are placed in a sealed container at a low temperature, no measurable amount of \( \text{NH}_3 \) is produced. Explain.

<table>
<thead>
<tr>
<th>Even though the reaction is spontaneous at low temperature, the reaction is very slow. The speed of a reaction depends on the fraction of colliding molecules with energy that exceeds the activation energy for the reaction. At low temperature, few reactant particles collide with an energy greater than the activation energy.</th>
<th>1 point for indicating that the frequency of collision (or kinetic energy) of molecules is low at low temperature (thus the rate is slow)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 point for indicating that at low temperature the kinetic energy will likely be too small to exceed the activation energy</td>
<td>1 point for indicating that the frequency of collision (or kinetic energy) of molecules is low at low temperature (thus the rate is slow)</td>
</tr>
</tbody>
</table>

---

Copyright © 2003 by College Entrance Examination Board. All rights reserved.
Available at apcentral.collegeboard.com.
N₂(g) + 2 H₂(g) ⇌ N₂H₄(g) \hspace{1cm} \Delta H_{298}^\circ = +95.4 \text{ kJ mol}^{-1}; \hspace{0.5cm} \Delta S_{298}^\circ = -176 \text{ J K}^{-1} \text{ mol}^{-1}

7. Answer the following questions about the reaction represented above using principles of thermodynamics.

(a) On the basis of the thermodynamic data given above, compare the sum of the bond strengths of the reactants to the sum of the bond strengths of the product. Justify your answer.

| Bond energy (B.E.) of reactants is greater than bond energy of products. Reaction is endothermic, so more energy is required to break bonds of reactants than is given off when new bonds form in products: \hspace{1cm} \Delta H = \sum (\text{B.E.})_{\text{reactants}} - \sum (\text{B.E.})_{\text{products}} > 0 | 1 point for indicating that reactants have greater bond strength | 1 point for correct explanation |

(b) Does the entropy change of the reaction favor the reactants or the product? Justify your answer.

| Entropy change favors reactants. Since there are three moles of reactants in gas phase compared to only one mole of products, there are more possible arrangements of reactant molecules compared to product molecules. | 1 point for indicating which, reactants or products, are favored | 1 point for explanation |

(c) For the reaction under the conditions specified, which is favored, the reactants or the product? Justify your answer.

| Reactants are favored because \( \Delta G^\circ \) for reaction is positive. \( \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \), so a positive \( \Delta H^\circ \) and a negative \( \Delta S^\circ \) means \( \Delta G^\circ \) is always positive, independent of temperature. Note: Calculation of \( \Delta G^\circ \) is acceptable with explanation. | 1 point for indicating which, reactants or products, are favored | 1 point for explanation |
(d) Explain how to determine the value of the equilibrium constant, $K_{eq}$, for the reaction. (Do not do any calculations.)

<table>
<thead>
<tr>
<th>Solve formula $\Delta G^\circ = -RT \ln K_{eq}$ for $K_{eq}$ and plug in value of $\Delta G^\circ$ calculated in part (c), value of temperature (298 K), and value of $R$ (8.31 J mol$^{-1}$ K$^{-1}$).</th>
<th>1 point for correct mathematical equation and substitution</th>
</tr>
</thead>
</table>

(e) Predict whether the value of $K_{eq}$ for the reaction is greater than 1, equal to 1, or less than 1. Justify your answer.

<table>
<thead>
<tr>
<th>$K_{eq}$ value is less than 1 for the reaction as written. $\Delta G^\circ = -RT \ln K_{eq}$, and since $\Delta G^\circ$ is positive, $\ln K_{eq}$ will be a negative number which means that $K_{eq}$ is less than one. OR $\Delta H^\circ &gt; 0$ and $S^\circ &lt; 0$, thus $\Delta G^\circ &gt; 0$, which means that $K_{eq} &lt; 1$.</th>
<th>1 point for the correct prediction with an explanation</th>
</tr>
</thead>
</table>
#3 \rightarrow 9 \text{ pts total}

1. \text{ DH}_{\text{B.E.}} = \text{ Bonds broken} - \text{ bonds formed} = 1 \text{ pt}
   \[ \text{C}_2\text{H}_5\text{Cl} + \text{Cl-Cl} \rightarrow \text{C}_2\text{H}_4\text{Cl}_2 + \text{HCl} \]
   \[
   \begin{array}{c}
   2794 & 243 & \text{2757} & 431 \\
   3037 & 3188 \hline
   \end{array}
   \]
   \[
   3037 - 3188 = -151 \text{ KJ/mol} \]

2. \text{ net}
   \[ \text{C-H} + \text{Cl-Cl} \rightarrow \text{C-Cl} + \text{HCl} \]
   \[
   \begin{array}{c}
   414 & 443 & -377 & 431 \\
   \hline
   \end{array}
   \]
   \[ DH = -151 \text{ KJ/mol} \]

3. \[
   \begin{align*}
   \Delta G &= \Delta G^0_{\text{C}_2\text{H}_4\text{Cl}_2} + \Delta G_{\text{HCl}} \\
   &= \left[ \Delta G^0_{\text{C}_2\text{H}_4\text{Cl}_2} + \Delta G_{\text{HCl}} \right] \\
   &= \left[ -80.3 - 95.3 \right] - \left[ -80.3 + 0 \right] = -115 \text{ KJ/mol}
   \end{align*}
   \]

4. 1 \text{ pt}
   \[
   \Delta G = DH - T\Delta S
   \]
   \[
   \Delta S = -151 \text{ KJ/mol} - (-115 \text{ KJ/mol}) = -120 \text{ KJ/mol}\cdot K
   \]

5. 1 \text{ pt}
   \[
   \ln K = \frac{-115,100 \text{ J/mol}\cdot K}{(8.314)(298)}
   \]
   \[
   K = 1.5 \times 10^{-20}
   \]

6. 1 \text{ pt}
   \[
   \begin{align*}
   \Delta G &= -RT \ln K \\
   \ln K &= \frac{115,100 \text{ J/mol}\cdot K}{(8.314)(298)}
   \end{align*}
   \]

7. 1 \text{ pt}
   \[
   \begin{align*}
   K &= 1.5 \times 10^{-20} \\
   \ln K &= -46.46
   \end{align*}
   \]

D. c) \text{ Keq} \checkmark + \text{ correct rationale}

a) \text{ Le Chatelier reasoning} \text{ OK} \Rightarrow \checkmark

b) \text{ a DBV from } \Delta G = DH - T\Delta S
   \text{ so } -RT \ln K \checkmark, \text{ etc}

8. 2 \text{ pts}

8. 4 \text{ pts}

C. = 2 \text{ pts}

D. = 1 \text{ pt}
Cl₂(g) + 3 F₂(g) → 2 ClF₃(g)

ClF₃ can be prepared by the reaction represented by the equation above. For ClF₃, the standard enthalpy of formation, ΔH°, is −163.2 kilojoules/mole and the standard free energy of formation, ΔG°, is −123.0 kilojoules/mole.

(a) Calculate the value of the equilibrium constant for the reaction at 298 K.
(b) Calculate the standard entropy change, ΔS°, for the reaction at 298 K.
(c) If ClF₃ were produced as a liquid rather than as a gas, how would the sign and magnitude of ΔS for the reaction be affected? Explain.
(d) At 298 K, the absolute entropies of Cl₂(g) and ClF₃(g) are 222.96 joules per mole-Kelvin and 281.50 joules per mole-Kelvin, respectively.

(i) Account for the larger entropy of ClF₃(g) relative to that of Cl₂(g).
(ii) Calculate the value of the absolute entropy of F₂(g) at 298 K.

(a) \[ \Delta G° = -RT \ln K \]
\[ \Delta G° = -246,000 \times (-8.314) \times 298 \text{ J/K} \]
\[ K = 1.32 \times 10^{-43} \]

(b) \[ \Delta G° = \Delta H° - T\Delta S° \]
\[ \Delta G° = -246,000 - 326,500 \times 298 \text{ J/K} \]
\[ \Delta S° = -270 \text{ J/K} \]

(c) \[ \Delta S° is a larger negative \]
(less disordered)

ClF₃ (g) is more ordered than Cl₂ (g).

(d) Entropy of ClF₃ > Entropy of Cl₂ because:
1) larger no. of atoms on
2) more complex particle or
3) more degrees of freedom

\[ \Delta S_{\text{rxn}} = \Delta S_{\text{prod}} - \Delta S_{\text{reactants}} \]
\[ -270 = 2(291.5) - (222.96 + 3SE₂) \]
\[ SE₂ = 203 \text{ J/K} \]

15
QUESTION 2
(9 pts.)

a) \[ \text{C}_2\text{H}_8 + 5 \text{O}_2 \rightarrow 3 \text{CO}_2 + 4 \text{H}_2\text{O} \]  

Notes: ignore phases (even when wrong)
multiples are OK
if balanced wrong, parts b and c should be consistent

b) \[ \frac{10.0 \text{ g C}_2\text{H}_8 \times 1 \text{ mol C}_2\text{H}_8}{44.1 \text{ g C}_2\text{H}_8} = 0.227 \text{ mol C}_2\text{H}_8 \]  

\[ \frac{0.227 \text{ mol C}_2\text{H}_8 \times 1 \text{ mol O}_2}{5 \text{ mol O}_2} = 1.13 \text{ mol O}_2 \]  

\[ \nu = \frac{(1.13 \text{ mol O}_2) (0.0821 \text{ L-atm \cdot mol}^{-1} \text{-K}^{-1}) (303 \text{ K})}{1.00 \text{ atm}} = 28.1 \text{ L O}_2 \]  

\[ 28.1 \text{ L O}_2 \times \frac{100 \text{ L air}}{21.0 \text{ L O}_2} = 134 \text{ L air} \]  

Note: answer must be consistent with part a

c) \[ \Delta H^o_{\text{rxn}} = \sum \Delta H^o_\text{f} (\text{products}) - \sum \Delta H^o_\text{f} (\text{reactants}) \]  

\[ -2220.1 \text{ kJ} = [4(-285.3 \text{ kJ}) + 3(-393.5 \text{ kJ})] - [5(0 \text{ kJ}) + \Delta H^o_\text{f} \text{(C}_2\text{H}_8)] \]  

\[ -2220.1 \text{ kJ} = -1141.2 \text{ kJ} - 1180.5 \text{ kJ} - \Delta H^o_\text{f} \text{(C}_2\text{H}_8) \]  

\[ -2220.1 \text{ kJ} = -2321.7 \text{ kJ} - \Delta H^o_\text{f} \text{(C}_2\text{H}_8) \]  

\[ -101.6 \text{ kJ} = \Delta H^o_\text{f} \text{(C}_2\text{H}_8) \]  

Notes: answer should be consistent with part a
1 point deducted if negative sign missing from answer
1 point deducted if \(-2220.1 \text{ kJ substituted for } \Delta H^o_\text{f} \text{(C}_2\text{H}_8)\)
no points earned if coefficients are inconsistent and not set equal to \(\Delta H^o\)

d) \[ \frac{30.0 \text{ g C}_2\text{H}_8 \times 1 \text{ mol C}_2\text{H}_8}{44.1 \text{ g C}_2\text{H}_8} \times \frac{2220.1 \text{ kJ}}{1 \text{ mol C}_2\text{H}_8} = 1.51 \times 10^3 \text{ kJ} \]  

\[ 1.51 \times 10^3 \text{ kJ} = 1.51 \times 10^6 \text{ J} = (8,000 \text{ g})(4.18 \text{ J-}^\text{g}^{-1} \text{-K}^{-1})(\Delta T) \]  

\[ 45.1 \text{ K} \text{ (or } ^\circ\text{C}) = \Delta T \]  

Notes: must correctly substitute into \(q = mc\Delta T\) for 1 point
1 point earned if \(q\) value wrong but \(\Delta T\) consistent
(a) \[ 2.000 \text{ g} \times \frac{1 \text{ mol}}{94.113 \text{ g}} = 0.02125 \text{ mol phenol} \]

Heat released per mole = \( \frac{64.98 \text{ kJ}}{0.02125 \text{ mol}} = 3,058 \text{ kJ/mol} \)

or, \( \Delta H_{\text{comb}} = -3,058 \text{ kJ/mol} \)

* Units not necessary

(b) \( \Delta H_{\text{comb}} = -3,058 \text{ kJ/mol} \)

\[ -3,058 \text{ kJ} = [6(-395.5) + 3(-285.85)] - [\Delta H_f^\circ \text{ phenol}] \]

\( \Delta H_f^\circ \text{ phenol} = -161 \text{ kJ} \)

* One point earned for correct sign of heat of combustion, one point for correct use of moles/coefficients, and one point for correct substitution

(c) \( \Delta S^\circ = [3(69.91) + 6(213.6)] [7(205.0) + 144.0] = -87.67 \text{ J/K} \)

\( \Delta G^\circ = \Delta H^\circ - T \Delta S^\circ = 3,058 \text{ kJ} - (298 \text{ K})(-0.08767 \text{ kJ/K}) = -3,032 \text{ kJ} \)

* Units not necessary; no penalty if correct except for wrong \( \Delta H_{\text{comb}} \) from part (a)

(d) moles gas = \( 9 \times [\text{moles from part (a)}] \)

\[ = 9(0.02125 \text{ mol}) = 0.1913 \text{ moles gas} \]

\( P = \frac{nRT}{V} = \frac{(0.1913 \text{ mol})(0.0821 \text{ L atm mol}^{-1} \text{ K}^{-1})(383 \text{ K})}{10.0 \text{ L}} = 0.601 \text{ atm} \)

* Units necessary; no penalty for using Celsius temperature if also lost point in part (c) for same error
Total Score 10 points

3. In an experiment, a sample of an unknown, pure gaseous hydrocarbon was analyzed. Results showed that the sample contained 6.000 g of carbon and 1.344 g of hydrogen.

(a) Determine the empirical formula of the hydrocarbon.

\[
\begin{align*}
n_C &= 6.000 \text{ g C} \left(\frac{1 \text{ mol C}}{12.00 \text{ g C}}\right) = 0.5000 \text{ mol C} \\
n_H &= 1.344 \text{ g H} \left(\frac{1 \text{ mol H}}{1.008 \text{ g H}}\right) = 1.333 \text{ mol H} \\
0.5000 \text{ mol C} &\quad 1.333 \text{ mol H} \\
0.5000 &\quad 0.5000 \\
1 \text{ mol C} : 2.667 \text{ mol H} \\
3 (1 \text{ mol C} : 2.667 \text{ mol H}) &= 3 \text{ mol C} : 8.000 \text{ mol H} \\
\text{The empirical formula is } C_3H_8
\end{align*}
\]

1 point for number of moles of carbon and number of moles of hydrogen

1 point for ratio of moles of carbon to moles of hydrogen

1 point for correct formula

(b) The density of the hydrocarbon at 25°C and 1.09 atm is 1.96 g L\(^{-1}\).

(i) Calculate the molar mass of the hydrocarbon.

\[
P V = nRT \\
P V = \frac{\text{grams}}{\text{molar mass}} \cdot \frac{RT}{P} \\
\text{molar mass} = \frac{\text{grams} \cdot RT}{P} \\
\text{molar mass} = 1.96 \text{ g L}^{-1} \cdot \frac{0.0821 \text{ L atm mol}^{-1} \text{ K}^{-1}}{298 \text{ K}} \cdot \frac{1.09 \text{ atm}}{1} \\
\text{molar mass} = 44.0 \text{ g mol}^{-1} \\
1.96 \text{ g L}^{-1} \times 22.4 \text{ L mol}^{-1} = 43.9 \text{ g mol}^{-1} \quad (1 \text{ point maximum})
\]

1 point for correct substitution and 1 point for answer

OR

1 point for calculation and 1 point for units

(ii) Determine the molecular formula of the hydrocarbon.

\[
\text{Empirical mass} \times n = \text{molar mass} \\
\text{Empirical mass for } C_3H_8 \text{ is } 44 \text{ g mol}^{-1} \\
44 \text{ g mol}^{-1} \times n = 44 \text{ g mol}^{-1} \Rightarrow n = 1, \text{ so the molecular formula is the same as the empirical formula, } C_3H_8
\]

1 point for reporting correct formula with verification
In another experiment, liquid heptane, $\text{C}_7\text{H}_{16}(l)$, is completely combusted to produce $\text{CO}_2(g)$ and $\text{H}_2\text{O}(l)$, as represented by the following equation.

$$\text{C}_7\text{H}_{16}(l) + 11 \text{ O}_2(g) \rightarrow 7 \text{ CO}_2(g) + 8 \text{ H}_2\text{O}(l)$$

The heat of combustion, $\Delta H_{\text{comb}}^\circ$, for one mole of $\text{C}_7\text{H}_{16}(l)$ is $-4.85 \times 10^3$ kJ.

(c) Using the information in the table below, calculate the value of $\Delta H_f^\circ$ for $\text{C}_7\text{H}_{16}(l)$ in kJ mol$^{-1}$.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\Delta H_f^\circ$ (kJ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{CO}_2(g)$</td>
<td>$-393.5$</td>
</tr>
<tr>
<td>$\text{H}_2\text{O}(l)$</td>
<td>$-285.8$</td>
</tr>
</tbody>
</table>

$\Delta H_f^\circ$ for $\text{C}_7\text{H}_{16}(l)$ is $-191$ kJ mol$^{-1}$.

(d) A 0.0108 mol sample of $\text{C}_7\text{H}_{16}(l)$ is combusted in a bomb calorimeter.

(i) Calculate the amount of heat released to the calorimeter.

$$q_{\text{released}} = 0.0108 \text{ mol C}_7\text{H}_{16} \left( \frac{-4850 \text{ kJ}}{1 \text{ mol C}_7\text{H}_{16}} \right) = 52.4 \text{ kJ of heat released}$$

(ii) Given that the total heat capacity of the calorimeter is 9.273 kJ °C$^{-1}$, calculate the temperature change of the calorimeter.

$$Q = C_p \Delta T$$

$$52.4 \text{ kJ} = 9.273 \text{ kJ °C}^{-1} \times \Delta T$$

$$\Delta T = \left( \frac{52.4 \text{ kJ}}{9.273 \text{ kJ °C}^{-1}} \right) = 5.65^\circ \text{C}$$

$$\Delta T = (52.4 \text{ kJ})(9.273 \text{ kJ °C}^{-1}) = +5.65^\circ \text{C}$$
2 Fe(s) + \frac{3}{2} O_2(g) \rightarrow Fe_2O_3(s) \quad \Delta H_f^\circ = -824 \text{ kJ mol}^{-1}

Iron reacts with oxygen to produce iron(III) oxide, as represented by the equation above. A 75.0 g sample of Fe(s) is mixed with 11.5 L of O_2(g) at 2.66 atm and 298 K.

(a) Calculate the number of moles of each of the following before the reaction begins.

(i) Fe(s)

\[ n_{\text{Fe}} = \frac{75.0 \text{ g Fe}}{55.85 \text{ g Fe}} \times \frac{1 \text{ mol Fe}}{1.34 \text{ mol Fe}} = 0.56 \text{ mol Fe} \]

1 point for number of moles of Fe(s)

(ii) O_2(g)

\[ PV = nRT \]
\[ n_{O_2} = \frac{PV}{RT} = \frac{2.66 \text{ atm} \times 11.5 \text{ L}}{0.0821 \text{ L atm mol}^{-1} \text{ K}^{-1} \times 298 \text{ K}} = 1.25 \text{ mol O}_2 \]

1 point for number of moles of O_2(g)

(b) Identify the limiting reactant when the mixture is heated to produce Fe_2O_3(s). Support your answer with calculations.

\[ n_{O_2} \text{ reacting} = 1.34 \text{ mol Fe} \times \frac{1.5 \text{ mol } O_2}{2 \text{ mol Fe}} = 1.01 \text{ mol } O_2 \]

There is 1.25 mol O_2 initially, so there is an excess of O_2, and Fe is the limiting reactant.

1 point for identifying limiting reactant

OR

\[ n_{\text{Fe}} \text{ reacting} = 1.25 \text{ mol O}_2 \times \frac{2 \text{ mol Fe}}{1.5 \text{ mol O}_2} = 1.67 \text{ mol Fe} \]

There is 1.34 mol Fe initially, so there is not enough Fe, and O_2 is the limiting reactant.

1 point for supporting calculation
(c) Calculate the number of moles of Fe$_2$O$_3$(s) produced when the reaction proceeds to completion.

\[
n_{\text{Fe}_2\text{O}_3} = 1.34 \text{ mol Fe} \times \frac{1 \text{ mol Fe}_2\text{O}_3}{2 \text{ mol Fe}} = 0.670 \text{ mol Fe}_2\text{O}_3
\]

1 point for number of moles of Fe$_2$O$_3$ produced

(d) The standard free energy of formation, $\Delta G^o_f$, of Fe$_2$O$_3$(s) is $-740$. kJ mol$^{-1}$ at 298 K.

(i) Calculate the standard entropy of formation, $\Delta S^o_f$, of Fe$_2$O$_3$(s) at 298 K. Include units with your answer.

\[
\Delta G^o_f = \Delta H^o_f - T \Delta S^o_f
\]

\[
-740 \text{ kJ mol}^{-1} = -824 \text{ kJ mol}^{-1} - (298 \text{ K}) \Delta S^o_f
\]

\[
+84 \text{ kJ mol}^{-1} = -(298 \text{ K}) \Delta S^o_f
\]

\[
\Delta S^o_f = \frac{+84 \text{ kJ mol}^{-1}}{-298 \text{ K}} = -0.28 \text{ kJ mol}^{-1} \text{ K}^{-1}
\]

1 point for calculation of $\Delta S^o_f$

1 point for correct units

(ii) Which is more responsible for the spontaneity of the formation reaction at 298 K, the standard enthalpy of formation, $\Delta H^o_f$, or the standard entropy of formation, $\Delta S^o_f$? Justify your answer.

$\Delta H^o_f$ is the more important factor. The reaction is exothermic, which favors spontaneity. $\Delta S^o_f$ is negative, which means the system becomes more ordered as the reaction proceeds. Greater order will not increase the spontaneity of the reaction.

1 point for indicating that $\Delta H^o_f$ is responsible

and for an explanation that addresses the signs of $\Delta H^o$ and $\Delta S^o$. 
The reaction represented below also produces iron(III) oxide. The value of $\Delta H^\circ$ for the reaction is $-280$ kJ per mole of Fe$_2$O$_3$(s) formed.

$$2 \text{FeO(s)} + \frac{1}{2} \text{O}_2(g) \rightarrow \text{Fe}_2\text{O}_3(s)$$

(e) Calculate the standard enthalpy of formation, $\Delta H_f^\circ$, of FeO(s).

| $\Delta H_{rxn}^\circ = \Sigma \Delta H_f^\circ$ (products) $- \Sigma \Delta H_f^\circ$ (reactants) | 1 point for correct stoichiometry |
| $\Delta H_{rxn}^\circ = \Delta H_f^\circ \text{Fe}_2\text{O}_3(s) - [2 \Delta H_f^\circ \text{FeO(s)} + \frac{1}{2} \Delta H_f^\circ \text{O}_2(g)]$ |  |
| $-280$ kJ mol$^{-1} = -824$ kJ mol$^{-1} - [2 \Delta H_f^\circ \text{FeO(s)} + \frac{1}{2}(0)]$ |  |
| $+544$ kJ mol$^{-1} = -2 \Delta H_f^\circ \text{FeO(s)}$ | 1 point for correct calculation |
| $-272$ kJ mol$^{-1} = \Delta H_f^\circ \text{FeO(s)}$ |  |
3. Answer the following questions about the thermodynamics of the reactions represented below.

Reaction X: \( \frac{1}{2} I_2(s) + \frac{1}{2} Cl_2(g) \rightleftharpoons ICl(g) \)
\[ \Delta H_f^\circ = 18 \text{ kJ mol}^{-1}, \quad \Delta S_f^\circ = 78.1 \text{ J K}^{-1} \text{ mol}^{-1} \]

Reaction Y: \( \frac{1}{2} I_2(s) + \frac{1}{2} Br_2(l) \rightleftharpoons IBr(g) \)
\[ \Delta H_f^\circ = 41 \text{ kJ mol}^{-1}, \quad \Delta S_f^\circ = 124 \text{ J K}^{-1} \text{ mol}^{-1} \]

(a) Is reaction X, represented above, spontaneous under standard conditions? Justify your answer with a calculation.

\[
\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = (18 \text{ kJ mol}^{-1}) - (298 \text{ K})(0.078 \text{ kJ mol}^{-1} \text{ K}^{-1}) = -5 \text{ kJ mol}^{-1}
\]
Reaction is spontaneous because \( \Delta G^\circ < 0 \).

One point is earned for the correct value of \( \Delta G^\circ \).
One point is earned for a correct justification of spontaneity.

(b) Calculate the value of the equilibrium constant, \( K_{eq} \), for reaction X at 25°C.

\[
\Delta G^\circ = -RT \ln K_{eq} \Rightarrow \ln K_{eq} = -\frac{\Delta G^\circ}{RT} \]
\[
\ln K_{eq} = \frac{(-5 \text{ kJ mol}^{-1})(10^3 \text{ J kJ}^{-1})}{(8.31 \text{ J mol}^{-1} \text{ K}^{-1})(298 \text{ K})} = 2.019
\]
\[ K_{eq} = e^{2.019} = (7.5314) = 8 \]

One point is earned for the correct answer.

(c) What effect will an increase in temperature have on the equilibrium constant for reaction X? Explain your answer.

\[
\Delta G^\circ = -RT \ln K_{eq} = \Delta H^\circ - T\Delta S^\circ \Rightarrow \ln K_{eq} = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}
\]
Since \( \Delta H^\circ \) is positive, an increase in \( T \) will cause \(-\Delta H^\circ/RT\) to become a smaller negative number, therefore \( K_{eq} \) will increase.

**OR**

The reaction is endothermic (\( \Delta H = +18 \text{ kJ mol}^{-1} \)); an increase in temperature shifts the reaction to favor more products relative to the reactants, resulting in an increase in the value of \( K_{eq} \).

One point is earned for the correct choice with a correct explanation.
(d) Explain why the standard entropy change is greater for reaction \( Y \) than for reaction \( X \).

<table>
<thead>
<tr>
<th>Both reaction ( X ) and reaction ( Y ) have solid iodine as a reactant, but the second reactant in reaction ( X ) is chlorine gas whereas the second reactant in reaction ( Y ) is liquid bromine. Liquids have lower entropies than gases, thus in reaction ( Y ) the reactants are more ordered (and have lower entropies) than in reaction ( X ). The products of both reaction ( X ) and reaction ( Y ) have about the same disorder, so the change in entropy from reactants to products is greater in reaction ( Y ) than in reaction ( X ).</th>
</tr>
</thead>
<tbody>
<tr>
<td>One point is earned for a correct explanation.</td>
</tr>
</tbody>
</table>

(e) Above what temperature will the value of the equilibrium constant for reaction \( Y \) be greater than 1.0? Justify your answer with calculations.

\[
\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \\
K_{eq} = 1 \text{ when } \Delta G^\circ = 0 \Rightarrow T\Delta S^\circ = \Delta H^\circ \Rightarrow \\
T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{41 \text{ kJ mol}^{-1}}{0.124 \text{ kJ mol}^{-1}\text{K}^{-1}} = 330 \text{ K} \\
\text{So when } T > 330 \text{ K, } \Delta G^\circ < 0 \text{ kJ mol}^{-1} \Rightarrow K_{eq} > 1.0
\]

One point is earned for \( \Delta G^\circ = 0 \).

One point is earned for the correct temperature.

(f) For the vaporization of solid iodine, \( I_2(s) \rightarrow I_2(g) \), the value of \( \Delta H_{298}^\circ \) is 62 kJ mol\(^{-1}\). Using this information, calculate the value of \( \Delta H_{298}^\circ \) for the reaction represented below.

\[
I_2(g) + Cl_2(g) \rightleftharpoons 2 \text{ICl(g)}
\]

\[
\begin{align*}
I_2(s) + Cl_2(g) & \rightleftharpoons 2 \text{ ICl(g)} & \Delta H_{298}^\circ = 2 \times 18 \text{ kJ mol}^{-1} \\
I_2(g) & \rightarrow I_2(s) & \Delta H_{298}^\circ = -62 \text{ kJ mol}^{-1} \\
I_2(g) + Cl_2(g) & \rightleftharpoons 2 \text{ ICl(g)} & \Delta H_{298}^\circ = -26 \text{ kJ mol}^{-1}
\end{align*}
\]

One point is earned for \( \Delta H_{298}^\circ \) of either the first or second equation.

One point is earned for the correct sum of the \( \Delta H_{298}^\circ \) values.