2019

AP® CollegeBoard

AP® Chemistry

Sample Student Responses and Scoring Commentary

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Question 2

Answer the following questions relating to the chemistry of the halogens.

(a) The molecular formulas of diatomic bromine, chlorine, fluorine, and iodine are written below. Circle the formula of the molecule that has the longest bond length. Justify your choice in terms of atomic structure.

Br_2 Cl_2 F_2 I_2

I_2 has the longest bond length because the radius of the I atom is greater than the radii of the other halogen atoms. Thus, the distance between the nuclei of atoms in I_2 is greater than it is in smaller halogens.	1 point is earned for circling I_2 and providing a valid explanation.

A chemistry teacher wants to prepare Br_2. The teacher has access to the following three reagents: $NaBr(aq)$, $Cl_2(g)$, and $I_2(s)$.

Half-Reaction	$E°$ at 25°C (V)
$Br_2 + 2\,e^- \rightarrow 2\,Br^-$	1.07
$Cl_2 + 2\,e^- \rightarrow 2\,Cl^-$	1.36
$I_2 + 2\,e^- \rightarrow 2\,I^-$	0.53

(b) Using the data in the table above, write the balanced equation for the thermodynamically favorable reaction that will produce Br_2 when the teacher combines two of the reagents. Justify that the reaction is thermodynamically favorable by calculating the value of $E°$ for the reaction.

$2\,Br^- + Cl_2 \rightarrow Br_2 + 2\,Cl^-$ $E° = E°(\text{reduced species}) - E°(\text{oxidized species})$ $= 1.36\text{ V} - 1.07\text{ V} = +0.29\text{ V}$. Because $E°$ for the reaction has a positive value, the reaction is thermodynamically favorable.	1 point is earned for the correct balanced equation. 1 point is earned for the correct calculation of $E°$.

Br_2 and Cl_2 can react to form the compound BrCl.

(c) The boiling point of Br_2 is 332 K, whereas the boiling point of BrCl is 278 K. Explain this difference in boiling point in terms of all the intermolecular forces present between molecules of each substance.

Question 2 (continued)

The only intermolecular attractions in $Br_2(l)$ are London forces, while those in $BrCl(l)$ include both London forces and dipole-dipole forces. However, due to the greater polarizability of the electron cloud of Br_2 compared to that of BrCl, the London forces in $Br_2(l)$ are stronger than the combined intermolecular forces in $BrCl(l)$. Thus, the boiling point of $Br_2(l)$ is greater than that of $BrCl(l)$.	1 point is earned for identifying the intermolecular forces in each substance. 1 point is earned for a valid explanation.

The compound BrCl can decompose into Br_2 and Cl_2, as represented by the balanced chemical equation below.

$$2\ BrCl(g) \rightleftarrows Br_2(g) + Cl_2(g) \qquad \Delta H° = 1.6\ \text{kJ/mol}_{rxn}$$

A 0.100 mole sample of pure $BrCl(g)$ is placed in a previously evacuated, rigid 2.00 L container at 298 K. Eventually the system reaches equilibrium according to the equation above.

(d) Calculate the pressure in the container before equilibrium is established.

$P = \frac{nRT}{V} = \frac{(0.100\ \text{mol})(0.08206\ \text{L atm mol}^{-1}\ \text{K}^{-1})(298\ \text{K})}{2.00\ \text{L}} = 1.22\ \text{atm}$	1 point is earned for a correct pressure with consistent units.

(e) Write the expression for the equilibrium constant, K_{eq}, for the decomposition of BrCl.

$K_{eq} = \frac{[Br_2][Cl_2]}{[BrCl]^2}$ or $K_{eq} = \frac{P_{Br_2} P_{Cl_2}}{(P_{BrCl})^2}$	1 point is earned for a correct equilibrium expression.

After the system has reached equilibrium, 42 percent of the original BrCl sample has decomposed.

(f) Determine the value of K_{eq} for the decomposition reaction of BrCl at 298 K.

$$2\ BrCl(g) \rightleftarrows Br_2(g) + Cl_2(g)$$

	$2\ BrCl(g)$	$Br_2(g)$	$Cl_2(g)$
I	1.22	0	0
C	$-2x$	$+x$	$+x$
E	0.71	0.26	0.26

1 point is earned for correct stoichiometric values at equilibrium.

P_{BrCl} decomposed $= (0.42)(1.22\ \text{atm}) = 0.51\ \text{atm}$

$2x = 0.51\ \text{atm} \Rightarrow x = 0.26\ \text{atm}$

$$K_{eq} = \frac{(0.26)(0.26)}{(0.71)^2} = 0.13$$

1 point is earned for a consistent value of K_{eq}.

Note: The solution is in terms of pressures. Solutions in terms of molar concentrations also earn full credit.

Question 2 (continued)

(g) Calculate the bond energy of the Br-Cl bond, in kJ/mol, using $\Delta H°$ for the reaction (1.6 kJ/mol$_{rxn}$) and the information in the following table.

Bond	Bond Energy (kJ/mol)
Br – Br	193
Cl – Cl	243
Br – Cl	?

$\Delta H° = \Sigma$ (bond energies)$_{broken}$ – Σ (bond energies)$_{formed}$ 1.6 kJ/mol = 2(Br–Cl bond energy) – (193 kJ/mol + 243 kJ/mol) (436 + 1.6) kJ/mol = 2(Br–Cl bond energy) Br–Cl bond energy = 219 kJ/mol	1 point is earned for a correct calculation of the Br–Cl bond energy.

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a) I_2 has the longest bond length because each bonded atom of I has a large atomic radius due to its greater number of electron orbits. This increases the distance between the bonded I atoms and makes the bond longer.

b) $Cl_2 + 2e^- \rightarrow 2Cl^-$ $E° = 1.07$ V

$+\ 2Br^- \rightarrow Br_2 + 2e^-$ $E° = -1.36$ V

$Cl_2 + 2Br^- \rightarrow 2Cl^- + Br_2$ $.29$ V

$E°$ (.29 V) is positive, so $\Delta G°$ is negative and the reaction is thermodynamically favorable

c) Br_2 has London dispersion forces only while BrCl has London dispersion forces and some dipole-dipole forces due to the electronegativity difference between Br and Cl. However, the greater London dispersion forces between larger Br_2 molecules are stronger than the combined London dispersion and dipole-dipole forces between BrCl molecules, so the boiling point of Br_2 is higher.

d) $PV = nRT$ $P = \frac{(.100\ mol)(.0821\ \frac{L \cdot atm}{mol \cdot K})(298\ K)}{2.00\ L}$

$P = \frac{nRT}{V}$

$P = 1.22$ atm

e) $K_{eq} = \frac{[Br_2][Cl_2]}{[BrCl]^2}$

f) $2BrCl_{(g)} \rightleftharpoons Br_{2(g)} + Cl_{2(g)}$ $.42(.05\ M) = .021\ M$

	$2BrCl$	Br_2	Cl_2
I	.05 M	0 M	0 M
C	−.021 M	+.0105 M	+.0105 M
E	.029 M	.0105 M	.0105 M

$K_{eq} = \frac{[.0105][.0105]}{[.029]^2} = .131$

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g) $\Delta H^\circ_{RXN} = \Sigma H^\circ_{\text{bonds broken}} - \Sigma H^\circ_{\text{bonds formed}}$

$1.6 \text{ kJ/mol} = 2(x) - [193 \text{ kJ/mol} + 243 \text{ kJ/mol}]$

$438 \text{ kJ/mol} = 2x$

$x = \boxed{219 \text{ kJ/mol}}$

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a) I_2 has the largest bond length because it has the largest atomic radius since it has the most shells.

b) $2NaBr + Cl_2 \longrightarrow Br_2 + 2NaCl$

$2Br^- \rightarrow Br_2 + 2e^-$ $\quad E° = -1.07$

$Cl_2 + 2e^- \rightarrow 2Cl^-$ $\quad E° = 1.36$

$1.36 - 1.07 = 0.29$

$E°_{rxn} = 0.29$

$\Delta G° = -nFE°$ ∴

If $E°_{rxn}$ is positive, $\Delta G°$ will be negative, and the reaction will be spontaneous.

c) Between molecules of Br_2, there are London Dispersion forces present, and there are also London dispersion forces present between molecules of BrCl. Br_2 has a higher boiling point than BrCl because the intermolecular forces between Br_2 molecules are stronger since Br_2 has more electrons than BrCl.

d) $\frac{PV}{V} = \frac{nRT}{V}$

$P = \frac{nRT}{V} = \frac{0.100\ mol \cdot 0.08206\ \frac{L\,atm}{mol \cdot K} \cdot 298\ K}{2.00\ L}$

P = 1.22 atm

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e) $K_{eq} = \frac{[Br_2][Cl_2]}{[BrCl]^2}$

f)

	2BrCl	Br_2	Cl_2
I	0.05M	0	0
C	$-2x = (0.42 \times 0.05) = -0.021$	$+x$	$+x$
E	$0.05 - 0.021$	0.0105	0.0105

$$K_{eq} = \frac{[Br_2][Cl_2]}{[BrCl]^2} = \frac{(0.0105)^2}{(0.029)^2}$$

$K_{eq} = 0.13$

g) $2(Br-Cl) - (Br-Br) - (Cl-Cl) = 1.6$ kJ/mol

$2(Br-Cl) = 1.6 + (Br-Br) + (Cl-Cl)$

$2(Br-Cl) = 1.6 + 193 + 243$

$\frac{2(Br-Cl)}{2} = \frac{438}{2}$

$\Delta H = 219$ kJ/mol

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2C 1 of 3

2. Answer the following questions relating to the chemistry of the halogens.

(a) The molecular formulas of diatomic bromine, chlorine, fluorine, and iodine are written below. Circle the formula of the molecule that has the longest bond length. Justify your choice in terms of atomic structure.

Br_2 Cl_2 F_2 I_2

A chemistry teacher wants to prepare Br_2. The teacher has access to the following three reagents: NaBr(aq), $Cl_2(g)$, and $I_2(s)$.

Half-Reaction	$E°$ at 25°C (V)
$Br_2 + 2e^- \rightarrow 2Br^-$	1.07
$Cl_2 + 2e^- \rightarrow 2Cl^-$	1.36
$I_2 + 2e^- \rightarrow 2I^-$	0.53

(b) Using the data in the table above, write the balanced equation for the thermodynamically favorable reaction that will produce Br_2 when the teacher combines two of the reagents. Justify that the reaction is thermodynamically favorable by calculating the value of $E°$ for the reaction.

Br_2 and Cl_2 can react to form the compound BrCl.

(c) The boiling point of Br_2 is 332 K, whereas the boiling point of BrCl is 278 K. Explain this difference in boiling point in terms of all the intermolecular forces present between molecules of each substance.

The compound BrCl can decompose into Br_2 and Cl_2, as represented by the balanced chemical equation below.

$$2\,BrCl(g) \rightleftarrows Br_2(g) + Cl_2(g) \qquad \Delta H° = 1.6\ kJ/mol_{rxn}$$

0.100 mole

A 0.100 mole sample of pure BrCl(g) is placed in a previously evacuated, rigid 2.00 L container at 298 K. Eventually the system reaches equilibrium according to the equation above.

(d) Calculate the pressure in the container before equilibrium is established.

(e) Write the expression for the equilibrium constant, K_{eq}, for the decomposition of BrCl.

After the system has reached equilibrium, 42 percent of the original BrCl sample has decomposed.

(f) Determine the value of K_{eq} for the decomposition reaction of BrCl at 298 K.

(g) Calculate the bond energy of the Br-Cl bond, in kJ/mol, using $\Delta H°$ for the reaction (1.6 kJ/mol$_{rxn}$) and the information in the following table.

Bond	Bond Energy (kJ/mol)
Br – Br	193
Cl – Cl	243
Br – Cl	?

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~~a) I_2 because it is the largest molecule. Therefore, it has less effective nuclear charge~~

a) F_2, because it is the smallest ~~molecule~~ atom, and F is the most electronegative of all the other atoms. Therefore, it can push away from the other F atom the most, making the longest bond length.

b) ~~$Br_2 + 2e^- \rightarrow 2Br^-$ $E_0 = 1.07V$~~

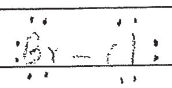
$2Br^- \longrightarrow Br_2 + 2e^-$ $E_0 = -1.07$

$Cl_2 + 2e^- \rightarrow 2Cl^-$ $E_0 = 1.38$

$Cl_2 + 2Br^- \rightarrow Br_2 + 2Cl^-$ $E^\circ = 0.29V$

c) $Br_2 \rightarrow$ London Dispersion forces

$BrCl \rightarrow$ London dispersion force.



Br_2 has a greater LDF because of its high polarizability than BrCl.

d) $PV = nRT$

$$P = \frac{nRT}{V} = \frac{(2)(0.100\ mol)\left(0.08206 \frac{L \cdot atm}{mol \cdot K}\right)(298\ K)}{2.00\ L}$$

$= \boxed{2.45\ atm}$

e) $K_{eq} = \frac{[Br_2][Cl_2]}{[BrCl]^2}$

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f) R $2BrCl \rightleftharpoons Br_2 + Cl_2$

I 0.1 0 0

C $-2x$ $+x$ $+x$

E $0.1-2x$ x x

$K_{eq} = \frac{(x)(x)}{(0.1-2x)^2}$

g) $\Delta H^\circ = [[Br-Br] + [Cl-Cl]] - [2Br-Cl]$

$1.6 = (193+243) - [2Br-Cl]$

$2Br-Cl = 436-1.6$

$2Br-Cl = 434.4$

$Br-Cl = \frac{434.4}{2}$

$Br-Cl = 217.2 \frac{kJ}{mol}$

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Question 2

Note: Student samples are quoted verbatim and may contain spelling and grammatical errors.

Overview

Question 2 incorporates a wide range of concepts (atomic structure, intermolecular forces, equilibrium) within the context of elemental halogens and the interhalogen compound BrCl. This question also highlights electrochemistry, the ideal gas law, and bond dissociation enthalpy.

In part (a) students are asked which among four elemental halogen compounds has the longest bond length. They must make a correct selection and justify their choice in terms of atomic structure (LO 2.21; SP 1.4). Part (b) provides a table of half-reactions, with standard potentials, for the reduction of various elemental halogen compounds. The student must use this information to write a balanced chemical equation for the thermodynamically favorable preparation of Br_2 and justify the favorability by calculating $E°$ for the process (LO 3.12; SP 2.2, 6.4). The intent is for students to recognize that only one of the reagents can oxidize Br^- to Br_2 in a thermodynamically favorable reaction (i.e., positive value of $E°$).

In part (c) students are asked to explain the difference between the boiling points of Br_2 and BrCl. They need to identify the intermolecular forces present between molecules of each substance and use that information to explain why Br_2 has a higher boiling point than BrCl (LO 5.9; SP 6.4). Part (d) requires a calculation of the initial pressure of BrCl(g) reactant in a rigid container prior to its decomposition into $Br_2(g)$ and $Cl_2(g)$. Students should use the ideal gas law and report the pressure in units that are consistent with the version of the gas constant R that they use (LO 2.6; SP 2.2). After equilibrium is established, students must write the expression for the equilibrium constant in part (e) and then determine the value of that constant in part (f) (LO 6.5; SP 2.2). Either a K_c or K_p expression is appropriate in this case. Part (g) gives a partial table of bond dissociation enthalpies and asks the student, given $\Delta H°$ for the reaction, to calculate the bond energy of the Br–Cl bond (LO 5.8; SP 2.3, 7.1, 7.2). Students must use Hess's law to find this missing value.

Sample: 2A
Score: 10

This response earned 10 out of 10 possible points. The student earned 1 point in part (a) for stating I_2 has the largest bond length since iodine has the largest atomic radius. The response earned 2 points in part (b) for a correct balanced redox equation, cell potential, $E°$, and states the reaction is thermodynamically favorable because $E°$ is a positive value. The response earned 2 points in part (c): The first point was earned for stating Br_2 has London dispersion forces and BrCl has London dispersion forces and weak dipole-dipole interactions. The second point was earned by stating that the London dispersion forces in Br_2 are stronger than the combined forces (London dispersion and dipole-dipole) in BrCl. The response earned 1 point in part (d) for the correct pressure calculation of the BrCl. The response earned 1 point in part (e) for the correct equilibrium constant, K_{eq}, in terms of concentration. Both points were earned for part (f). The student calculates the correct stoichiometric equilibrium values of BrCl, Br_2, and Cl_2 and the correct value of the equilibrium concentration, K_c. The response earned 1 point in part (g) for correctly determining the bond energy of BrCl from the bond energies provided.

Sample: 2B
Score: 9

This response earned 9 out of 10 possible points. The student earned 1 point in part (a) for choosing I_2 and stating iodine has the largest atomic radius since it has the most shells. Part (b) earned 2 points for a correct balanced equation, cell potential, $E°$, and stating the reaction is thermodynamically favorable because $E°$ is positive. One

Question 2 (continued)

point was earned in part (c). The first point was not earned; the student incorrectly identifies only London dispersion forces in BrCl. The second point was earned for stating the intermolecular forces are stronger in Br_2 than BrCl. The response earned 1 point in part (d) for the correct pressure of BrCl and 1 point in part (e) for the correct K_{eq}. Two points were earned in part (f). The student correctly calculates the equilibrium values of BrCl, Br_2, and Cl_2 ,as well as the K_{eq}. Part (g) earned 1 point for the correct calculation of the BrCl bond energy.

Sample: 2C
Score: 4

This response earned 4 out of 10 possible points. In part (a) no point was earned for stating that F_2 has the largest bond length. The response earned 2 points in part (b):1 point for the correctly balanced equation and 1 point for the correct value of $E°$. One of 2 points was earned for part (c). The student incorrectly states that BrCl has only London dispersion forces (LDF) but correctly states the LDFs in Br_2 are stronger than BrCl; thus, the student earned the second point. Part (d) earned no points. The student incorrectly multiplies the number of moles by 2 when calculating the pressure of BrCl. The response earned 1 point in part (e) for the correct K_{eq} expression. No points were earned for part (f). The student does not determine the equilibrium values or calculate for K_{eq}. Part (g) earned no points. The student reverses the terms in the relationship between the enthalpy change for the reaction and the bond energies of the reactants and the products (i.e., equating the enthalpy change to Σ(bond energies)$_{formed}$ – Σ(bond energies)$_{broken}$).