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.
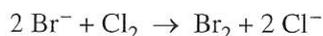
$$Br_2 \qquad Cl_2 \qquad F_2 \qquad I_2$$

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.

$$2\,Br^- + Cl_2 \rightarrow Br_2 + 2\,Cl^-$$ $E° = E°(\text{reduced species}) - E°(\text{oxidized species})$ $\quad = 1.36\text{ V} - 1.07\text{ V} = +0.29\text{ V}.$ 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 <u>each</u> substance.

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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.

$$2\ BrCl(g) \rightleftharpoons Br_2(g) + Cl_2(g) \qquad \Delta H° = 1.6\ kJ/mol_{rxn}$$
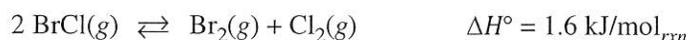
A 0.100 mole sample of pure $BrCl(g)$ is placed in a previously evacuated, rigid 2.00 L container at 298 K. Eventually the system reaches equilibrium according to the equation above.

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

$P = \dfrac{nRT}{V} = \dfrac{(0.100\ mol)(0.08206\ L\ atm\ mol^{-1}\ K^{-1})(298\ K)}{2.00\ L} = 1.22\ atm$	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.

$K_{eq} = \dfrac{[Br_2][Cl_2]}{[BrCl]^2}$ or $K_{eq} = \dfrac{P_{Br_2} P_{Cl_2}}{(P_{BrCl})^2}$	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.

$2\ BrCl(g) \rightleftharpoons Br_2(g) + Cl_2(g)$ <table><tr><td>I</td><td>1.22</td><td>0</td><td>0</td></tr><tr><td>C</td><td>−2x</td><td>+x</td><td>+x</td></tr><tr><td>E</td><td>0.71</td><td>0.26</td><td>0.26</td></tr></table> P_{BrCl} decomposed = (0.42)(1.22 atm) = 0.51 atm $2x = 0.51\ atm \Rightarrow x = 0.26\ atm$ $K_{eq} = \dfrac{(0.26)(0.26)}{(0.71)^2} = 0.13$ Note: The solution is in terms of pressures. Solutions in terms of molar concentrations also earn full credit.	1 point is earned for correct stoichiometric values at equilibrium. 1 point is earned for a consistent value of K_{eq}.

(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	?

$\Delta H° = \sum$ (bond energies)$_{broken} - \sum$ (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.