CHEMISTRY
Section II

YOU MAY USE YOUR CALCULATOR FOR SECTION II.

CLEARLY SHOW THE METHOD USED AND THE STEPS INVOLVED IN ARRIVING AT YOUR ANSWERS. It is to your advantage to do this, since you may obtain partial credit if you do and you will receive little or no credit if you do not. Attention should be paid to significant figures.

1. A sample of solid U_3O_8 (*s*) is placed in a rigid 1.500 L flask. Chlorine gas, $Cl_2(g)$, is added, and. the flask is heated to 862°C. The equation for the reaction that takes place and the equilibrium-constant expression for the reaction are given below.

$$U_3O_8(s) + 3\ Cl_2(g) \leftrightarrows 3\ UO_2Cl_2(g) + O_2(g) \qquad K_p = \frac{(P_{UO_2Cl_2})^3(P_{O_2})}{(P_{Cl_2})^3}$$

When the system is at equilibrium, the partial pressure of $Cl_2(g)$ is 1.007 atm and the partial pressure of $UO_2Cl_2(g)$ is 9.734×10^{-4} atm.

(a) Calculate the partial pressure of O_2(g) at equilibrium at 862°C.

(b) Calculate the value of the equilibrium constant, K_p, for the system at 862°C.

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(c) Calculate the Gibbs free-energy change, $\Delta G°$ for the reaction at 862°C.

(d) State whether the entropy change, $\Delta S°$ for the reaction at 862°C is positive, negative, or zero. Using particulate level reasoning explain your answer.

(e) State whether the enthalpy change, $\Delta H°$ for the reaction at 862°C is positive, negative or zero Justify your answer.

(f) After a certain period of time, 1.000 mol of $O_2(g)$ is added to the mixture in the flask. Does the mass of U_3O_8 (*s*) in the flask increase, decrease, or remain the same? Justify your answer.

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A sample of solid U_3O_8 (*s*) is placed in a rigid 1.500 L flask. Chlorine gas, $Cl_2(g)$, is added, and. the flask is heated to 862°C. The equation for the reaction that takes place and the equilibrium-constant expression for the reaction are given below.

$$U_3O_8(s) + 3\ Cl_2(g) \leftrightarrows 3\ UO_2Cl_2(g) + O_2(g) \qquad K_p = \frac{(P_{UO_2Cl_2})^3(P_{O_2})}{(P_{Cl_2})^3}$$

When the system is at equilibrium, the partial pressure of $Cl_2(g)$ is 1.007 atm and the partial pressure of UO_2Cl_2 (*g*) is 9.734×10^{-4} atm.

(a) Calculate the partial pressure of $O_2(g)$ at equilibrium at 862°C.

This part of the question is a stoichiometry question that can be solved with an ICE

	$U_3O_8(s)$	+	$3\ Cl_2(g)$	$\leftrightarrows$	$3\ UO_2Cl_2(g)$	+	$O_2(g)$
Initial (atm)					0		0
Change (atm)			-0.0009734		+ 0.0009734		+ 0.0003245
Equil (atm)			1.007		0.0009734		0.0003245

$$9.734\times10^{-4}\text{ atm }UO_2Cl_2 \times \frac{1\text{ mol }O_2}{3\text{ mol }UO_2Cl_2} = 3.245\times10^{-4}\text{ atm }O_2$$

1 point for the correct answer with work shown

(b) Calculate the value of the equilibrium constant, K_p, for the system at 862°C.

$$K_p = \frac{(P_{UO_2Cl_2})^3(P_{O_2})}{(P_{Cl_2})^3} \qquad K_p = \frac{(9.734\times10^{-4})^3(3.245\times10^{-4})}{(1.007)^3} = 2.931\times10^{-13}$$

One point is earned for the correct substitution

One point is earned for the correct answer

(c) Calculate the Gibbs free-energy change, $\Delta G°$ for the reaction at 862°C.

$\Delta G° = -RT\ln K_p$

$\Delta G° = -8.31\text{ J mol}^{-1} \times (862 + 273)\text{ K} \times \ln(2.931 \times 10^{-13}) = 272{,}000\text{ J mol}^{-1} = 272\text{ kJ mol}^{-1}$

One point is earned for the correct setup

One point is earned for the correct answer with units.

(d) State whether the entropy change, $\Delta S°$ for the reaction at 862°C is positive, negative, or zero. Using particulate level reasoning explain your answer.

$\Delta S°$ is positive because four mol of gaseous products are produced from three mol of gaseous reactants. Also, the particles in the products are free to move as gases, while some of the particles in the reactants are constrained in the solid phase.

One point is earned for the correct sign.

One point is for earned either explanation.

(e) State whether the enthalpy change, $\Delta H°$, for the reaction at 862°C is positive, negative or zero Justify your answer.

Both $\Delta G°$ and $\Delta S°$ are positive, as determined in parts (c) and (d). Thus $\Delta H°$ must be positive because $\Delta H°$ is the sum of two positive terms in the equation.

$$\Delta H° = \Delta G° + T\Delta S°$$

One point is earned for the correct sign.

One point is earned for the correct explanation.

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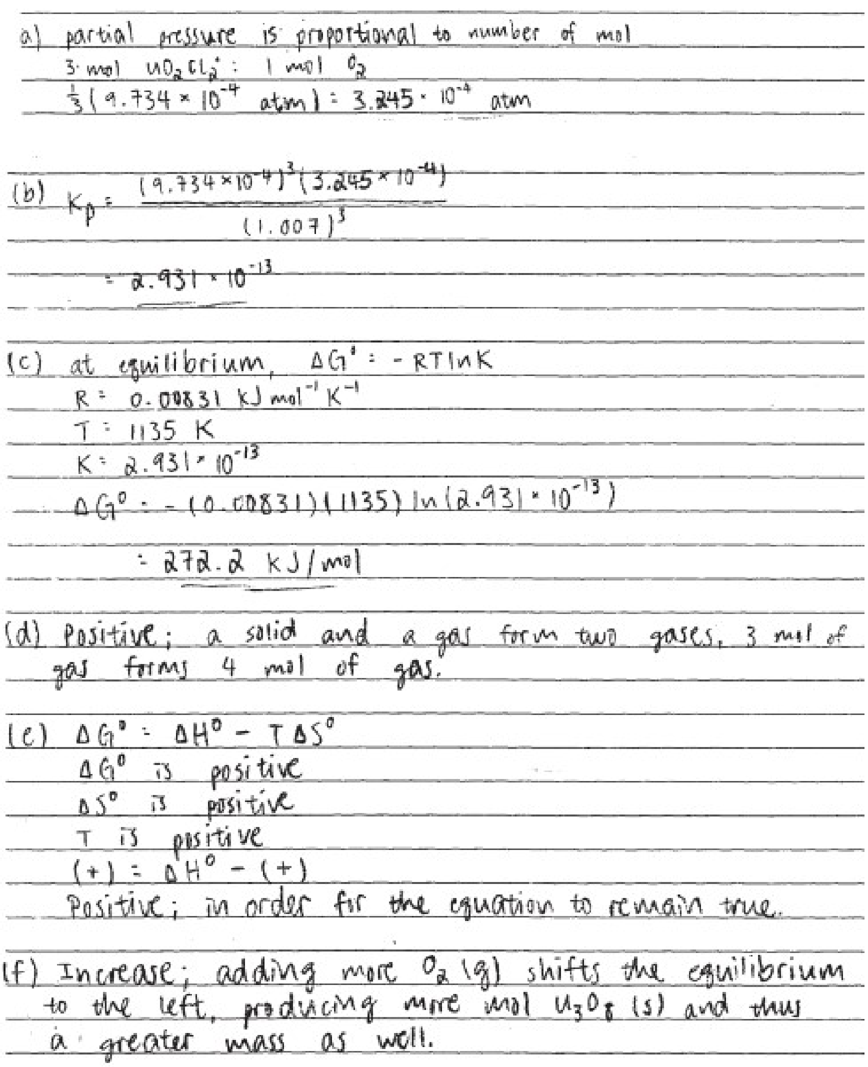
(f) After a certain period of time, 1.000 mol of $O_2(g)$ is added to the mixture in the flask. Does the mass of U_3O_8 (*s*) in the flask increase, decrease, or remain the same? Justify your answer. The mass of U_3O_8 will increase because the addition of a product creates as "stress" on the product (right) side of the reaction increasing the reaction quotient making *Q* greater than *K*. $Q = \frac{(P_{UO_2Cl_2})^3 (P_{O_2} \uparrow)}{(P_{Cl_2})^3}$ increases $Q > K$. The reaction will then proceed from the ← right to the left to reestablish equilibrium so that some UO_2Cl and $O_2(g)$ is consumed. As the product is consumed in the reverse reaction, more U_3O_8 (*s*) is produced $U_3O_8(s)\uparrow + 3\ Cl_2(g)\uparrow \leftarrow 3\ UO_2Cl_2(g)\downarrow + O_2\downarrow\ (g)$ until the reaction *Q* again equals *K*. Note student answer is shorter and still gets full credit.	One point is earned for the correct answer and justification.

Sample student answer receiving full credit.



a) partial pressure is proportional to number of mol
3 mol UO_2Cl_2 : 1 mol O_2
$\frac{1}{3}(9.734 \times 10^{-4}$ atm$) = 3.245 \times 10^{-4}$ atm

(b) $K_p = \frac{(9.734\times10^{-4})^3(3.245\times10^{-4})}{(1.007)^3}$
$= 2.931 \times 10^{-13}$

(c) at equilibrium, $\Delta G° = -RT\ln K$
$R = 0.00831$ kJ mol^{-1} K^{-1}
$T = 1135$ K
$K = 2.931 \times 10^{-13}$
$\Delta G° = -(0.00831)(1135)\ln(2.931 \times 10^{-13})$
$= 272.2$ kJ/mol

(d) Positive; a solid and a gas form two gases, 3 mol of gas forms 4 mol of gas.

(e) $\Delta G° = \Delta H° - T\Delta S°$
$\Delta G°$ is positive
$\Delta S°$ is positive
T is positive
$(+) = \Delta H° - (+)$
Positive; in order for the equation to remain true.

(f) Increase; adding more $O_2(g)$ shifts the equilibrium to the left, producing more mol $U_3O_8(s)$ and thus a greater mass as well.

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$N_2(g) + 3\ F_2(g) \rightarrow 2\ NF_3(g)$ $\Delta H^o_{298} = -264$ kJ mol_{rxn}^{-1} ; $\Delta S^o = -278$ J K^{-1} mol_{rxn}^{-1}

2. The following questions relate to the synthesis reaction represented by the chemical equation in the box above.

(a) Calculate the value of the standard free energy change, ΔG^o, for the reaction.

(b) The bond enthalpy for the three types of covalent bonds in this reaction are 156 kJ/mol, 272 kJ/mol, and 941 kJ/mol. Identify the bond energy for the N_2 molecules. Justify your answer.

(c) Calculate the standard enthalpy change, ΔH^o, that occurs when a 0.256 mol sample of $NF_3(g)$ is formed from $N_2(g)$ and $F_2(g)$ at 1.00 atm and 298 K.

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$N_2(g) + 3\ F_2(g) \rightarrow 2\ NF_3(g)$ ΔH^o_{298} = -264 kJ mol_{rxn}^{-1} ; ΔS^o = -278 J K^{-1} mol_{rxn}^{-1} 2. The following questions relate to the synthesis reaction represented by the chemical equation in the box above. (a) Calculate the value of the standard free energy change, ΔG^o_{298} , for the reaction. $\Delta G°_{298} = \Delta H°_{298} - T\Delta S°_{298}$ $\Delta G°$=-264 kJ mol^{-1} - 298 K × (-0.278 kJ K^{-1} mol^{-1}) $\Delta G°$= -181 kJ mol_{rxn}^{-1}	One point is earned for the value of $\Delta G°$ in J or kJ
(b) The bond enthalpy for the three types of covalent bonds in this reaction are 156 kJ/mol, 272 kJ/mol, and 941 kJ/mol. Identify the bond energy for the N_2 molecules. Justify your answer. The bond energy of the N_2 molecules was 941 kJ/mol because N_2 molecules have a sigma and two pi bonds, N ≡ N, while the F-F and N-F only have sigma bonds.	One point is earned for the identifying the N_2 as having the highest bond energy with the justification indicating the difference in the bonds.
(c) Calculate the standard enthalpy change, $\Delta H°$, that occurs when a 0.256 mol sample of $NF_3(g)$ is formed from $N_2(g)$ and $F_2(g)$ at 1.00 atm and 298 K. $N_2(g) + 3\ F_2(g) \rightarrow \mathbf{2\ NF_3}(g)$ ΔH^o_{298} = -264 kJ mol_{rxn}^{-1} $\Delta H°$ 2 mol NF_3(g) is -264 kJ $\dfrac{-264\text{ kJ}}{2.00\text{ mol}} \times 0.0256\text{ mol} = -3.38\text{ kJ}$	One point is earned for the correct answer with units.

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