CHEMISTRY

Section II

(Total time—95 minutes)

Part A

Time—55 minutes

YOU MAY USE YOUR CALCULATOR FOR PART A.

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.

Be sure to write all your answers to the questions on the lined pages following each question in the goldenrod booklet. Do NOT write your answers on the lavender insert.

Answer Questions 1, 2, and 3. The Section II score weighting for each question is 20 percent.

1. A sample of solid U_3O_8 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.

$$U_3O_8(s) + 3\,Cl_2(g) \rightleftarrows 3\,UO_2Cl_2(g) + O_2(g) \qquad K_p = \frac{(p_{UO_2Cl_2})^3(p_{O_2})}{(p_{Cl_2})^3}$$

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.

(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. Justify 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.

Question 1

A sample of solid U_3O_8 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.

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

$U_3O_8(s) + 3\,Cl_2(g) \rightleftarrows 3\,UO_2Cl_2(g) + O_2(g)$ I: --- ; ? ; 0 ; 0 C: E: ; 1.007 atm ; 9.734×10^{-4} atm ; ? 9.734×10^{-4} atm $UO_2Cl_2(g) \times \frac{(1 \text{ mol } O_2)}{(3 \text{ mol } UO_2Cl_2)} = 3.245 \times 10^{-4}$ atm $O_2(g)$	One point is earned for the correct answer.

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

$K_p = \frac{(p_{UO_2Cl_2})^3(p_{O_2})}{(p_{Cl_2})^3} = \frac{(9.734\times10^{-4})^3(3.245\times10^{-4})}{(1.007)^3} = 2.931 \times 10^{-13}$	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.

$\Delta G° = -RT \ln K_p$ $= (-8.31 \text{ J mol}^{-1}\text{ K}^{-1})((862+273)\text{ K})(\ln(2.931 \times 10^{-13}))$ $= 272{,}000 \text{ J mol}^{-1} = 272 \text{ kJ mol}^{-1}$	One point is earned for the correct setup. One point is earned for the correct answer with units.

Question 1 (continued)

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

$\Delta S°$ is positive because four moles of gaseous products are produced from three moles of gaseous reactants.	One point is earned for the correct 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 a correct explanation.

(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 $U_3O_8(s)$ will increase because the reaction is at equilibrium, and the addition of a product creates a "stress" on the product (right) side of the reaction. The reaction will then proceed from right to left to reestablish equilibrium so that some $O_2(g)$ is consumed (tending to relieve the stress) as more $U_3O_8(s)$ is produced.	One point is earned for a correct explanation.

1A,

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(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.

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$) = 3.245 \cdot 10^{-4}$ atm

GO ON TO THE NEXT PAGE.

1A2

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

$= 2.931\times10^{-13}$

(c) at equilibrium, $\Delta G° = -RT\ln K$

$R = 0.00831$ kJ $mol^{-1} K^{-1}$

$T = 1135$ K

$K = 2.931\times10^{-13}$

~~$\Delta G° = -(0.00831)(1135)\ln(2.931\times10^{-13})$~~

$= 272.2$ 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.

Question 1

Sample: 1A
Score: 9

This response earned all 9 points: 1 for part (a), 2 for part (b), 2 for part (c), 1 for part (d), 2 for part (e), and 1 for part (f).

Sample: 1B
Score: 6

The point was not earned in part (a) because the student incorrectly attempts to use the Ideal Gas Law to determine the partial pressure of O_2 gas at equilibrium. Both points were earned in part (b) because the student correctly substitutes and calculates a value for the equilibrium constant using the pressure calculated in part (a). Both points were earned in part (c) because the student correctly substitutes and calculates a value for $\Delta G°$ using the K_p from part (b). The point was earned in part (d). The first point was earned for part (e) because the student correctly identifies the sign of $\Delta H°$ as positive; however, the second point was not earned because the justification given relates to the heat added to start the reaction rather than a connection to the Gibb's equation. The point was not earned in part (f).

Sample: 1C
Score: 3

The point was not earned in part (a). Both points were earned in part (b) because the student correctly substitutes and calculates a value for the equilibrium constant using the calculated pressure from part (a). Only 1 point was earned in part (c) because although the student substitutes correctly, using the K_p value calculated in part (b), the incorrect R is used in the equation. No points were earned for parts (d), (e), or (f).