

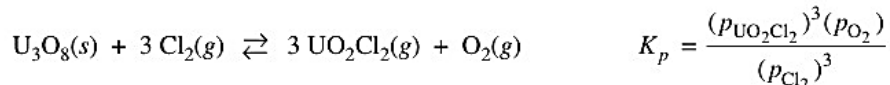
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2007B

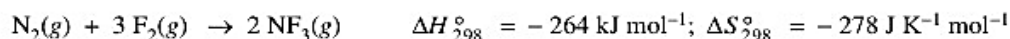
1. A sample of solid  $\text{U}_3\text{O}_8$  is placed in a rigid 1.500 L flask. Chlorine gas,  $\text{Cl}_2(g)$ , is added, and the flask is heated to  $862^\circ\text{C}$ . The equation for the reaction that takes place and the equilibrium-constant expression for the reaction are given below.



When the system is at equilibrium, the partial pressure of  $\text{Cl}_2(g)$  is 1.007 atm and the partial pressure of  $\text{UO}_2\text{Cl}_2(g)$  is  $9.734 \times 10^{-4}$  atm.

- Calculate the partial pressure of  $\text{O}_2(g)$  at equilibrium at  $862^\circ\text{C}$ .
- Calculate the value of the equilibrium constant,  $K_p$ , for the system at  $862^\circ\text{C}$ .
- Calculate the Gibbs free-energy change,  $\Delta G^\circ$ , for the reaction at  $862^\circ\text{C}$ .
- State whether the entropy change,  $\Delta S^\circ$ , for the reaction at  $862^\circ\text{C}$  is positive, negative, or zero. Justify your answer.
- State whether the enthalpy change,  $\Delta H^\circ$ , for the reaction at  $862^\circ\text{C}$  is positive, negative, or zero. Justify your answer.
- After a certain period of time, 1.000 mol of  $\text{O}_2(g)$  is added to the mixture in the flask. Does the mass of  $\text{U}_3\text{O}_8(s)$  in the flask increase, decrease, or remain the same? Justify your answer.

2007



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

- Calculate the value of the standard free energy change,  $\Delta G_{298}^\circ$ , for the reaction.
- Determine the temperature at which the equilibrium constant,  $K_{eq}$ , for the reaction is equal to 1.00. (Assume that  $\Delta H^\circ$  and  $\Delta S^\circ$  are independent of temperature.)
- Calculate the standard enthalpy change,  $\Delta H^\circ$ , that occurs when a 0.256 mol sample of  $\text{NF}_3(g)$  is formed from  $\text{N}_2(g)$  and  $\text{F}_2(g)$  at 1.00 atm and 298 K.

The enthalpy change in a chemical reaction is the difference between energy absorbed in breaking bonds in the reactants and energy released by bond formation in the products.

- How many bonds are formed when two molecules of  $\text{NF}_3$  are produced according to the equation in the box above?
- Use both the information in the box above and the table of average bond enthalpies below to calculate the average enthalpy of the F–F bond.

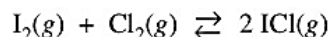
Bond	Average Bond Enthalpy (kJ mol <sup>-1</sup> )
N≡N	946
N–F	272
F–F	?

2006B

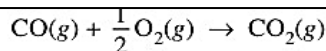
3. Answer the following questions about the thermodynamics of the reactions represented below.



- Is reaction *X*, represented above, spontaneous under standard conditions? Justify your answer with a calculation.
- Calculate the value of the equilibrium constant,  $K_{eq}$ , for reaction *X* at 25°C.
- What effect will an increase in temperature have on the equilibrium constant for reaction *X*? Explain your answer.
- Explain why the standard entropy change is greater for reaction *Y* than for reaction *X*.
- Above what temperature will the value of the equilibrium constant for reaction *Y* be greater than 1.0? Justify your answer with calculations.
- For the vaporization of solid iodine,  $\text{I}_2(s) \rightarrow \text{I}_2(g)$ , the value of  $\Delta H_{298}^\circ$  is 62 kJ mol<sup>-1</sup>. Using this information, calculate the value of  $\Delta H_{298}^\circ$  for the reaction represented below.



2006



2. The combustion of carbon monoxide is represented by the equation above.

- Determine the value of the standard enthalpy change,  $\Delta H_{rxn}^\circ$ , for the combustion of  $\text{CO}(g)$  at 298 K using the following information.

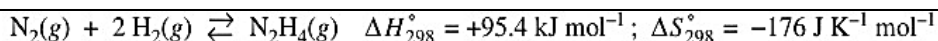


- Determine the value of the standard entropy change,  $\Delta S_{rxn}^\circ$ , for the combustion of  $\text{CO}(g)$  at 298 K using the information in the following table.

Substance	$S_{298}^\circ$ (J mol <sup>-1</sup> K <sup>-1</sup> )
CO(g)	197.7
CO <sub>2</sub> (g)	213.7
O <sub>2</sub> (g)	205.1

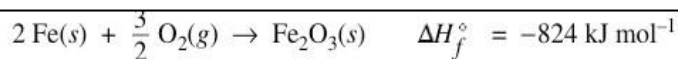
- Determine the standard free energy change,  $\Delta G_{rxn}^\circ$ , for the reaction at 298 K. Include units with your answer.
- Is the reaction spontaneous under standard conditions at 298 K? Justify your answer.
- Calculate the value of the equilibrium constant,  $K_{eq}$ , for the reaction at 298 K.

2004B



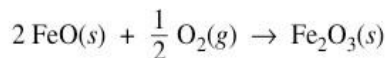
7. Answer the following questions about the reaction represented above using principles of thermodynamics .
- On the basis of the thermodynamic data given above, compare the sum of the bond strengths of the reactants to the sum of the bond strengths of the product. Justify your answer.
  - Does the entropy change of the reaction favor the reactants or the product? Justify your answer.
  - For the reaction under the conditions specified, which is favored, the reactants or the product? Justify your answer.
  - Explain how to determine the value of the equilibrium constant,  $K_{eq}$ , for the reaction. (Do not do any calculations.)
  - Predict whether the value of  $K_{eq}$  for the reaction is greater than 1, equal to 1, or less than 1. Justify your answer.

2004



2. 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<sub>2</sub>(g) at 2.66 atm and 298 K.
- Calculate the number of moles of each of the following before the reaction begins.
    - Fe(s)
    - O<sub>2</sub>(g)
  - Identify the limiting reactant when the mixture is heated to produce Fe<sub>2</sub>O<sub>3</sub>(s). Support your answer with calculations.
  - Calculate the number of moles of Fe<sub>2</sub>O<sub>3</sub>(s) produced when the reaction proceeds to completion.
  - The standard free energy of formation,  $\Delta G_f^\circ$ , of Fe<sub>2</sub>O<sub>3</sub>(s) is -740. kJ mol<sup>-1</sup> at 298 K.
    - Calculate the standard entropy of formation,  $\Delta S_f^\circ$ , of Fe<sub>2</sub>O<sub>3</sub>(s) at 298 K. Include units with your answer.
    - Which is more responsible for the spontaneity of the formation reaction at 298 K, the standard enthalpy of formation,  $\Delta H_f^\circ$ , or the standard entropy of formation,  $\Delta S_f^\circ$ ? Justify your answer.

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<sub>2</sub>O<sub>3</sub>(s) formed.

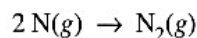


- Calculate the standard enthalpy of formation,  $\Delta H_f^\circ$ , of FeO(s).

2003

7. Answer the following questions that relate to the chemistry of nitrogen.

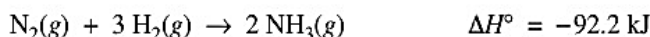
- (a) Two nitrogen atoms combine to form a nitrogen molecule, as represented by the following equation.



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

Bond	Average Bond Energy (kJ mol <sup>-1</sup> )
N — N	160
N = N	420
N ≡ N	950

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



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

- (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.
- (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  $\text{NH}_3(g)$  is produced. Explain.

2002B

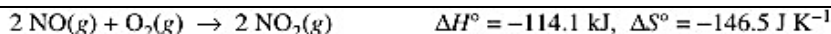
3. Nitrogen monoxide,  $\text{NO}(g)$ , and carbon monoxide,  $\text{CO}(g)$ , are air pollutants generated by automobiles. It has been proposed that under suitable conditions these two gases could react to form  $\text{N}_2(g)$  and  $\text{CO}_2(g)$ , which are components of unpolluted air.

- (a) Write a balanced equation for the reaction described above. Indicate whether the carbon in  $\text{CO}$  is oxidized or whether it is reduced in the reaction. Justify your answer.
- (b) Write the expression for the equilibrium constant,  $K_p$ , for the reaction.
- (c) Consider the following thermodynamic data.

	<u>NO</u>	<u>CO</u>	<u>CO<sub>2</sub></u>
$\Delta G_f^\circ$ (kJ mol <sup>-1</sup> )	+86.55	-137.15	-394.36

- (i) Calculate the value of  $\Delta G^\circ$  for the reaction at 298 K.
- (ii) Given that  $\Delta H^\circ$  for the reaction at 298 K is  $-746 \text{ kJ}$  per mole of  $\text{N}_2(g)$  formed, calculate the value of  $\Delta S^\circ$  for the reaction at 298 K. Include units with your answer.
- (d) For the reaction at 298 K, the value of  $K_p$  is  $3.3 \times 10^{120}$ . In an urban area, typical pressures of the gases in the reaction are  $P_{\text{NO}} = 5.0 \times 10^{-7} \text{ atm}$ ,  $P_{\text{CO}} = 5.0 \times 10^{-5} \text{ atm}$ ,  $P_{\text{N}_2} = 0.781 \text{ atm}$ , and  $P_{\text{CO}_2} = 3.1 \times 10^{-4} \text{ atm}$ .
- (i) Calculate the value of  $\Delta G$  for the reaction at 298 K when the gases are at the partial pressures given above.
- (ii) In which direction (to the right or to the left) will the reaction be spontaneous at 298 K with these partial pressures? Explain.

2001



2. The reaction represented above is one that contributes significantly to the formation of photochemical smog.
- (a) Calculate the quantity of heat released when 73.1 g of  $\text{NO}(g)$  is converted to  $\text{NO}_2(g)$ .
- (b) For the reaction at  $25^\circ\text{C}$ , the value of the standard free-energy change,  $\Delta G^\circ$ , is  $-70.4 \text{ kJ}$ .
- (i) Calculate the value of the equilibrium constant,  $K_{eq}$ , for the reaction at  $25^\circ\text{C}$ .
- (ii) Indicate whether the value of  $\Delta G^\circ$  would become more negative, less negative, or remain unchanged as the temperature is increased. Justify your answer.
- (c) Use the data in the table below to calculate the value of the standard molar entropy,  $S^\circ$ , for  $\text{O}_2(g)$  at  $25^\circ\text{C}$ .

	Standard Molar Entropy, $S^\circ$ ( $\text{J K}^{-1} \text{ mol}^{-1}$ )
$\text{NO}(g)$	210.8
$\text{NO}_2(g)$	240.1

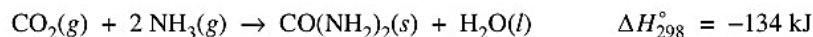
- (d) Use the data in the table below to calculate the bond energy, in  $\text{kJ mol}^{-1}$ , of the nitrogen-oxygen bond in  $\text{NO}_2$ . Assume that the bonds in the  $\text{NO}_2$  molecule are equivalent (i.e., they have the same energy).

	Bond Energy ( $\text{kJ mol}^{-1}$ )
Nitrogen-oxygen bond in $\text{NO}$	607
Oxygen-oxygen bond in $\text{O}_2$	495
Nitrogen-oxygen bond in $\text{NO}_2$	?

1999

6. Answer the following questions in terms of thermodynamic principles and concepts of kinetic molecular theory.

- (a) Consider the reaction represented below, which is spontaneous at  $298 \text{ K}$ .



- (i) For the reaction, indicate whether the standard entropy change,  $\Delta S_{298}^\circ$ , is positive, or negative, or zero. Justify your answer.
- (ii) Which factor, the change in enthalpy,  $\Delta H_{298}^\circ$ , or the change in entropy,  $\Delta S_{298}^\circ$ , provides the principal driving force for the reaction at  $298 \text{ K}$ ? Explain.
- (iii) For the reaction, how is the value of the standard free energy change,  $\Delta G^\circ$ , affected by an increase in temperature? Explain.
- (b) Some reactions that are predicted by their sign of  $\Delta G^\circ$  to be spontaneous at room temperature do not proceed at a measurable rate at room temperature.
- (i) Account for this apparent contradiction.
- (ii) A suitable catalyst increases the rate of such a reaction. What effect does the catalyst have on  $\Delta G^\circ$  for the reaction? Explain.