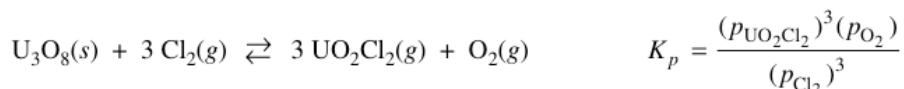


2007B

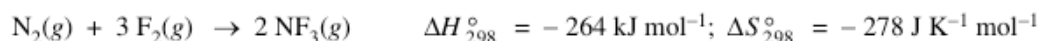
1. A sample of solid U_3O_8 is placed in a rigid 1.500 L flask. Chlorine gas, $\text{Cl}_2(g)$, is added, and the flask is heated to 862°C . The equation for the reaction that takes place and the equilibrium-constant expression for the reaction are given below.



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 9.734×10^{-4} atm.

- Calculate the partial pressure of $\text{O}_2(g)$ at equilibrium at 862°C .
- Calculate the value of the equilibrium constant, K_p , for the system at 862°C .
- Calculate the Gibbs free-energy change, ΔG° , for the reaction at 862°C .
- State whether the entropy change, ΔS° , for the reaction at 862°C is positive, negative, or zero. Justify your answer.
- State whether the enthalpy change, ΔH° , for the reaction at 862°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, ΔG_{298}° , for the reaction.
 - Determine the temperature at which the equilibrium constant, K_{eq} , for the reaction is equal to 1.00. (Assume that ΔH° and ΔS° are independent of temperature.)
 - Calculate the standard enthalpy change, ΔH° , 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.

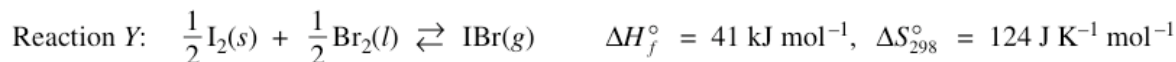
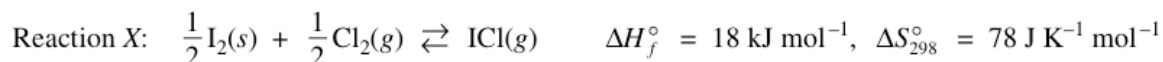
The enthalpy change in a chemical reaction is the difference between energy absorbed in breaking bonds in the reactants and energy released by bond formation in the products.

- How many bonds are formed when two molecules of 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 $\text{F}-\text{F}$ bond.

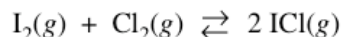
Bond	Average Bond Enthalpy (kJ mol ⁻¹)
$\text{N}\equiv\text{N}$	946
$\text{N}-\text{F}$	272
$\text{F}-\text{F}$?

2006B

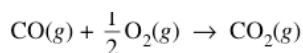
3. Answer the following questions about the thermodynamics of the reactions represented below.



- 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 ΔH_{298}° is 62 kJ mol⁻¹. Using this information, calculate the value of ΔH_{298}° 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, ΔH_{rxn}° , for the combustion of CO(g) at 298 K using the following information.

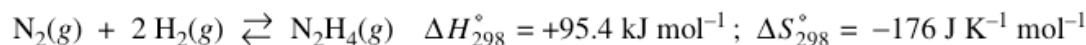


- Determine the value of the standard entropy change, ΔS_{rxn}° , for the combustion of CO(g) at 298 K using the information in the following table.

Substance	S_{298}° (J mol ⁻¹ K ⁻¹)
CO(g)	197.7
CO ₂ (g)	213.7
O ₂ (g)	205.1

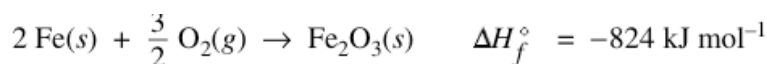
- Determine the standard free energy change, ΔG_{rxn}° , for the reaction at 298 K. Include units with your answer.
- Is the reaction spontaneous under standard conditions at 298 K? Justify your answer.
- Calculate the value of the equilibrium constant, K_{eq} , for the reaction at 298 K.

2004B



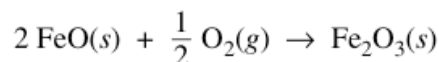
7. Answer the following questions about the reaction represented above using principles of thermodynamics .
- On the basis of the thermodynamic data given above, compare the sum of the bond strengths of the reactants to the sum of the bond strengths of the product. Justify your answer.
 - Does the entropy 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 $\text{O}_2(\text{g})$ at 2.66 atm and 298 K.
- Calculate the number of moles of each of the following before the reaction begins.
 - Fe(s)
 - $\text{O}_2(\text{g})$
 - Identify the limiting reactant when the mixture is heated to produce $\text{Fe}_2\text{O}_3(\text{s})$. Support your answer with calculations.
 - Calculate the number of moles of $\text{Fe}_2\text{O}_3(\text{s})$ produced when the reaction proceeds to completion.
 - The standard free energy of formation, ΔG_f° , of $\text{Fe}_2\text{O}_3(\text{s})$ is $-740. \text{ kJ mol}^{-1}$ at 298 K.
 - Calculate the standard entropy of formation, ΔS_f° , of $\text{Fe}_2\text{O}_3(\text{s})$ 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, ΔH_f° , or the standard entropy of formation, ΔS_f° ? Justify your answer.

The reaction represented below also produces iron(III) oxide. The value of ΔH° for the reaction is $-280. \text{ kJ}$ per mole of $\text{Fe}_2\text{O}_3(\text{s})$ formed.

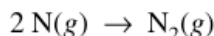


- Calculate the standard enthalpy of formation, ΔH_f° , of FeO(s).

2003

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

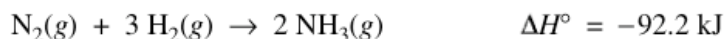
- (a) Two nitrogen atoms combine to form a nitrogen molecule, as represented by the following equation.



Using the table of average bond energies below, determine the enthalpy change, ΔH , for the reaction.

Bond	Average Bond Energy (kJ mol ⁻¹)
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, ΔS° , for the reaction. Justify your answer.

- (c) The value of ΔG° 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 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>CO₂</u>
ΔG_f° (kJ mol ⁻¹)	+86.55	-137.15	-394.36

- (i) Calculate the value of ΔG° for the reaction at 298 K.
- (ii) Given that ΔH° for the reaction at 298 K is -746 kJ per mole of $\text{N}_2(g)$ formed, calculate the value of ΔS° for the reaction at 298 K. Include units with your answer.
- (d) For the reaction at 298 K, the value of K_p is 3.3×10^{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 ΔG 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.



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°C , the value of the standard free-energy change, ΔG° , is -70.4 kJ .
- (i) Calculate the value of the equilibrium constant, K_{eq} , for the reaction at 25°C .
- (ii) Indicate whether the value of ΔG° 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° , for $\text{O}_2(g)$ at 25°C .

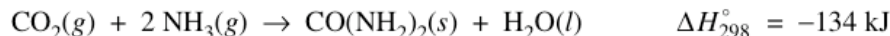
	Standard Molar Entropy, S° ($\text{J K}^{-1} \text{mol}^{-1}$)
$\text{NO}(g)$	210.8
$\text{NO}_2(g)$	240.1

- (d) Use the data in the table below to calculate the bond energy, in kJ mol^{-1} , of the nitrogen-oxygen bond in NO_2 . Assume that the bonds in the NO_2 molecule are equivalent (i.e., they have the same energy).

	Bond Energy (kJ mol^{-1})
Nitrogen-oxygen bond in NO	607
Oxygen-oxygen bond in O_2	495
Nitrogen-oxygen bond in NO_2	?

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 K .



- (i) For the reaction, indicate whether the standard entropy change, ΔS_{298}° , is positive, or negative, or zero. Justify your answer.
- (ii) Which factor, the change in enthalpy, ΔH_{298}° , or the change in entropy, ΔS_{298}° , provides the principal driving force for the reaction at 298 K ? Explain.
- (iii) For the reaction, how is the value of the standard free energy change, ΔG° , affected by an increase in temperature? Explain.
- (b) Some reactions that are predicted by their sign of ΔG° 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 ΔG° for the reaction? Explain.