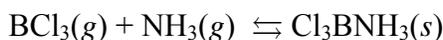


## Essay Questions

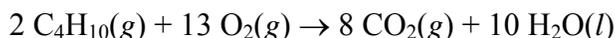
1991



The reaction represented above is a reversible reaction.

- Predict the sign of the entropy change,  $\Delta S$ , as the reaction proceeds to the right. Explain your prediction.
- If the reaction spontaneously proceeds to the right, predict the sign of the enthalpy change,  $\Delta H$ . Explain your prediction.
- The direction in which the reaction spontaneously proceeds changes as the temperature is increased above a specific temperature. Explain.
- What is the value of the equilibrium constant at the temperature referred to in (c); that is, the specific temperature at which the direction of the spontaneous reaction changes? Explain.

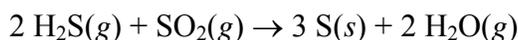
1993



The reaction represented above is spontaneous at 25°C. Assume that all reactants and products are in their standard state.

- Predict the sign of  $\Delta S^\circ$  for the reaction and justify your prediction.
- What is the sign of  $\Delta G^\circ$  for the reaction? How would the sign and magnitude of  $\Delta G^\circ$  be affected by an increase in temperature to 50°C? Explain your answer.
- What must be the sign of  $\Delta H^\circ$  for the reaction at 25°C? How does the total bond energy of the reactants compare to that of the products?
- When the reactants are placed together in a container, no change is observed even though the reaction is known to be spontaneous. Explain this observation.

1994



At 298 K, the standard enthalpy change,  $\Delta H^\circ$  for the reaction represented above is -145 kilojoules.

- Predict the sign of the standard entropy change,  $\Delta S^\circ$ , for the reaction. Explain the basis for your prediction.
- At 298 K, the forward reaction (*i.e.*, toward the right) is spontaneous. What change, if any, would occur in the value of  $\Delta G^\circ$  for this reaction as the temperature is increased? Explain your reasoning using thermodynamic principles.
- What change, if any, would occur in the value of the equilibrium constant,  $K_{eq}$ , for the situation described in (b)? Explain your reasoning.
- The absolute temperature at which the forward reaction becomes nonspontaneous can be predicted. Write the equation that is used to make the prediction. Why does this equation predict only an approximate value for the temperature?

1997

For the gaseous equilibrium represented below, it is observed that greater amounts of  $\text{PCl}_3$  and  $\text{Cl}_2$  are produced as the temperature is increased.

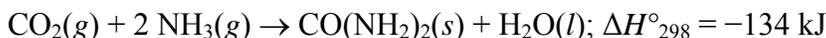


- What is the sign of  $\Delta S^\circ$  for the reaction? Explain.
- What change, if any, will occur in  $\Delta G^\circ$  for the reaction as the temperature is increased. Explain your reasoning in terms of thermodynamic principles.
- If He gas is added to the original reaction mixture at constant volume and temperature, what will happen to the partial pressure of  $\text{Cl}_2$ ? Explain.
- If the volume of the original reaction is decreased at constant temperature to half the original volume, what will happen to the number of moles of  $\text{Cl}_2$  in the reaction vessel? Explain.

1999

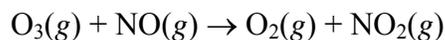
Answer the following questions in terms of thermodynamic principles and concepts of kinetic molecular theory.

- Consider the reaction represented below, which is spontaneous at 298 K.



- For the reaction, indicate whether the standard entropy change,  $\Delta S^\circ_{298}$ , is positive, or negative, or zero. Justify your answer.
  - Which factor, the change in enthalpy,  $\Delta H^\circ_{298}$ , or the change in entropy,  $\Delta S^\circ_{298}$ , provides the principal driving force for the reaction at 298 K? Explain.
  - For the reaction, how is the value of the standard free energy change,  $\Delta G^\circ$ , affected by an increase in temperature? Explain.
- 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.
    - Account for this apparent contradiction.
    - A suitable catalyst increases the rate of such a reaction. What effect does the catalyst have on  $\Delta G^\circ$  for the reaction? Explain.

2000



Consider the reaction represented above.

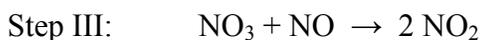
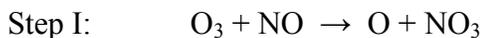
- (a) Referring to the data in the table below, calculate the standard enthalpy change,  $\Delta H^\circ$ , for the reaction at  $25^\circ\text{C}$ . Be sure to show your work.

	$\text{O}_3(g)$	$\text{NO}(g)$	$\text{NO}_2(g)$
Standard enthalpy of formation, $\Delta H_f^\circ$ , at $25^\circ\text{C}$ ( $\text{kJ mol}^{-1}$ )	143	90.	33

- (b) Make a qualitative prediction about the magnitude of the standard entropy change,  $\Delta S^\circ$ , for the reaction at  $25^\circ\text{C}$ . Justify your answer.
- (c) On the basis of your answers to parts (a) and (b), predict the sign of the standard free-energy change,  $\Delta G^\circ$ , for the reaction at  $25^\circ\text{C}$ . Explain your reasoning.
- (d) Use the information in the table below to write the rate-law expression for the reaction, and explain how you obtained your answer.

Experiment Number	Initial $[\text{O}_3]$ ( $\text{mol L}^{-1}$ )	Initial $[\text{NO}]$ ( $\text{mol L}^{-1}$ )	Initial Rate of Formation of $\text{NO}_2$ ( $\text{mol L}^{-1} \text{s}^{-1}$ )
1	0.0010	0.0010	$x$
2	0.0010	0.0020	$2x$
3	0.0020	0.0010	$2x$
4	0.0020	0.0020	$4x$

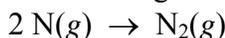
- (e) The following three-step mechanism is proposed for the reaction. Identify the step that must be the slowest in order for this mechanism to be consistent with the rate-law expression derived in part (d). Explain.



2003

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

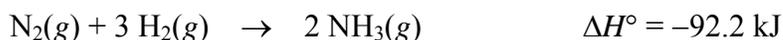
- (a) Two nitrogen atoms combine to form a nitrogen molecule, as represented by the following equation.



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

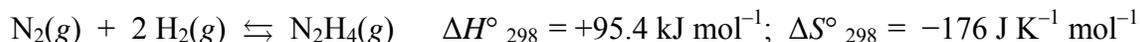
- (b) The reaction between nitrogen and hydrogen to form ammonia is represented below.



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.

2004B



Answer the following questions about the reaction represented above using principles of thermodynamics.

- (a) 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.
- (b) Does the entropy change of the reaction favor the reactants or the product? Justify your answer.
- (c) For the reaction under the conditions specified, which is favored, the reactants or the product? Justify your answer.
- (d) Explain how to determine the value of the equilibrium constant,  $K_{eq}$ , for the reaction. (Do not do any calculations.)
- (e) Predict whether the value of  $K_{eq}$  for the reaction is greater than 1, equal to 1, or less than 1. Justify your prediction.

## Problems

1990

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 Standard Free Energies of Formation at 298 K
 

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Substance	$\Delta G_f^\circ$ 298 K, kJ mol <sup>-1</sup>
C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub> (g)	-80.3
C <sub>2</sub> H <sub>5</sub> Cl(g)	-60.5
HCl(g)	-95.3
Cl <sub>2</sub> (g)	0

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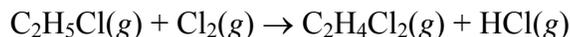
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 Average Bond Dissociation Energies at 298 K
 

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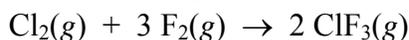
Bond	Energy, kJ mol <sup>-1</sup>
C-H	414
C-C	347
C-Cl	377
Cl-Cl	243
H-Cl	431

The tables above contain information for determining thermodynamic properties of the reaction below.



- Calculate the  $\Delta H^\circ$  for the reaction above, using the table of average bond dissociation energies.
- Calculate the  $\Delta S^\circ$  for the reaction at 298 K, using data from either table as needed.
- Calculate the value of  $K_{eq}$  for the reaction at 298 K.
- What is the effect of an increase in temperature on the value of the equilibrium constant? Explain your answer.

1992



ClF<sub>3</sub> can be prepared by the reaction represented by the equation above. For ClF<sub>3</sub> the standard enthalpy of formation,  $\Delta H_f^\circ$ , is -163.2 kilojoules/mole and the standard free energy of formation,  $\Delta G_f^\circ$ , is -123.0 kilojoules/mole.

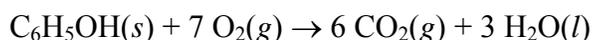
- Calculate the value of the equilibrium constant for the reaction at 298K.
- Calculate the standard entropy change,  $\Delta S^\circ$ , for the reaction at 298K.
- If ClF<sub>3</sub> were produced as a liquid rather than as a gas, how would the sign and the magnitude of  $\Delta S$  for the reaction be affected? Explain.
- At 298K the absolute entropies of Cl<sub>2</sub>(g) and ClF<sub>3</sub>(g) are 222.96 joules per mole · Kelvin and 281.50 joules per mole · Kelvin, respectively.
  - Account for the larger entropy of ClF<sub>3</sub>(g) relative to that of Cl<sub>2</sub>(g).
  - Calculate the value of the absolute entropy of F<sub>2</sub>(g) at 298K.

1995

Propane,  $C_3H_8$ , is a hydrocarbon that is commonly used as fuel for cooking.

- Write a balanced equation for the complete combustion of propane gas, which yields  $CO_2(g)$  and  $H_2O(l)$ .
- Calculate the volume of air at  $30^\circ C$  and 1.00 atmosphere that is needed to burn completely 10.0 grams of propane. Assume that air is 21.0 percent  $O_2$  by volume.
- The heat of combustion of propane is  $-2,220.1$  kJ/mol. Calculate the heat of formation,  $\Delta H_f^\circ$  of propane given that  $\Delta H_f^\circ$  of  $H_2O(l) = -285.3$  kJ/mol and  $\Delta H_f^\circ$  of  $CO_2(g) = -393.5$  kJ/mol.
- Assuming that all of the heat evolved in burning 30.0 grams of propane is transferred to 8.00 kilograms of water (specific heat =  $4.18$  J/gK), calculate the increase in temperature of water.

1998



When a 2.000-gram sample of pure phenol,  $C_6H_5OH(s)$ , is completely burned according to the equation above, 64.98 kilojoules of heat is released. Use the information in the table below to answer the questions that follow.

Substance	Standard Heat of Formation, $\Delta H_f^\circ$ , at $25^\circ C$ (kJ/mol)	Absolute Entropy, $S^\circ$ , at $25^\circ C$ (J/mol-K)
$C_{(graphite)}$	0.00	5.69
$CO_2(g)$	-395.5	213.6
$H_2(g)$	0.00	130.6
$H_2O(l)$	-285.85	69.91
$O_2(g)$	0.00	205.0
$C_6H_5OH(s)$	?	144.0

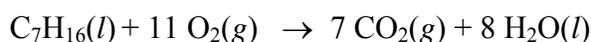
- Calculate the molar heat of combustion of phenol in kilojoules per mole at  $25^\circ C$ .
- Calculate the standard heat of formation,  $\Delta H_f^\circ$ , of phenol in kilojoules per mole at  $25^\circ C$ .
- Calculate the value of the standard free-energy change,  $\Delta G^\circ$  for the combustion of phenol at  $25^\circ C$ .
- If the volume of the combustion container is 10.0 liters, calculate the final pressure in the container when the temperature is changed to  $110^\circ C$ . (Assume no oxygen remains unreacted and that all products are gaseous.)

2003B

In an experiment, a sample of an unknown, pure gaseous hydrocarbon was analyzed. Results showed that the sample contained 6.000 g of carbon and 1.344 g of hydrogen.

- Determine the empirical formula of the hydrocarbon.
- The density of the hydrocarbon at 25°C and 1.09 atm is 1.96 g L<sup>-1</sup>.
  - Calculate the molar mass of the hydrocarbon.
  - Determine the molecular formula of the hydrocarbon.

In another experiment, liquid heptane, C<sub>7</sub>H<sub>16</sub>(l), is completely combusted to produce CO<sub>2</sub>(g) and H<sub>2</sub>O(l), as represented by the following equation.



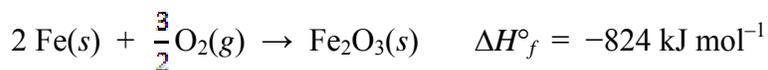
The heat of combustion,  $\Delta H^\circ_{\text{comb}}$ , for one mole of C<sub>7</sub>H<sub>16</sub>(l) is  $-4.85 \times 10^3$  kJ.

- Using the information in the table below, calculate the value of  $\Delta H^\circ_f$  for C<sub>7</sub>H<sub>16</sub>(l) in kJ mol<sup>-1</sup>.

Compound	$\Delta H^\circ_f$ (kJ mol <sup>-1</sup> )
CO <sub>2</sub> (g)	-393.5
H <sub>2</sub> O(l)	-285.8

- A 0.0108 mol sample of C<sub>7</sub>H<sub>16</sub>(l) is combusted in a bomb calorimeter.
  - Calculate the amount of heat released to the calorimeter.
  - Given that the total heat capacity of the calorimeter is 9.273 kJ °C<sup>-1</sup>, calculate the temperature change of the calorimeter.

2004

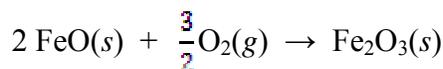


Iron reacts with oxygen to produce iron(III) oxide, as represented by the equation above. A 75.0 g sample of Fe(s) is mixed with 11.5 L of O<sub>2</sub>(g) at 2.66 atm and 298 K.

- 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.

- (c) Calculate the number of moles of  $\text{Fe}_2\text{O}_3(s)$  produced when the reaction proceeds to completion.
- (d) The standard free energy of formation,  $\Delta G^\circ_f$ , of  $\text{Fe}_2\text{O}_3(s)$  is  $-740. \text{ kJ mol}^{-1}$  at 298 K.
- (i) Calculate the standard entropy of formation,  $\Delta S^\circ_f$ , of  $\text{Fe}_2\text{O}_3(s)$  at 298 K. Include units with your answer.
- (ii) Which is more responsible for the spontaneity of the formation reaction at 298 K, the standard enthalpy of formation,  $\Delta H^\circ_f$ , or the standard entropy of formation,  $\Delta S^\circ_f$ ? Justify your answer.

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



Calculate the standard enthalpy of formation,  $\Delta H^\circ_f$ , of  $\text{FeO}(s)$ .

2006B

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



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

