

19.22 The element cesium (Cs) freezes at 28.4°C, and its molar enthalpy of fusion is  $\Delta H_{fus} = 2.09 \text{ kJ/mol}$  (a) When molten cesium solidifies to Cs(s) at its normal melting point, is  $\Delta S$  positive or negative? (b) Calculate the value of  $\Delta S$  when 15.0 g of Cs(l) solidifies at 28.4°C.

(a)  $\Delta S = -$

(b) 
$$\frac{15.0 \text{ g}}{132.9 \text{ g/mol}} \times \frac{2.09 \text{ kJ}}{\text{mol}} \times \frac{10^3 \text{ J}}{1 \text{ kJ}} = \frac{782 \text{ J}}{\text{K}}$$

19.44 Using Appendix C, compare the standard entropies at 25°C for the following pairs of substances: (a) CuO(s) and Cu<sub>2</sub>O(s); (b) 1 mol N<sub>2</sub>O<sub>4</sub>(g) and 2 mol NO<sub>2</sub>(g); (c) CH<sub>3</sub>OH(g) and CH<sub>3</sub>OH(l); (d) 1 mol PbO(s) plus 1 mol CO<sub>2</sub>(g) and 1 mol PbCO<sub>3</sub>(s). For each pair, explain the difference in the entropy values.

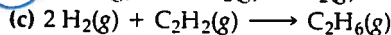
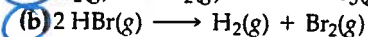
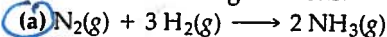
(a) Cu<sub>2</sub>O > CuO More disorganized  
More vibrational degrees of freedom

(b) 2 mol NO<sub>2</sub> > 1 mol N<sub>2</sub>O<sub>4</sub> (more molecules)

(c) CH<sub>3</sub>OH(g) > CH<sub>3</sub>OH(l)  
Molecules in gas occupy greater Vol

(d) PbO + CO<sub>2</sub> > PbCO<sub>3</sub> (same as b)

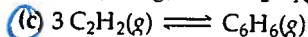
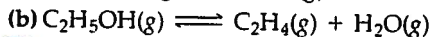
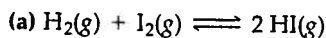
19.72 Indicate whether  $\Delta G$  increases, decreases, or does not change when the partial pressure of H<sub>2</sub> is increased in each of the following reactions:



(a)  $\Delta G = \Delta G^\circ + RT \ln Q$   

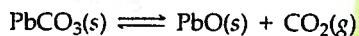
$$\frac{(\text{NH}_3)^2}{(\text{H}_2)^3 (\text{N}_2)^2}$$
 Q ↓  
 ΔG ↓  
 more neg  
 more spontaneous

19.75 Use data from Appendix C to calculate the equilibrium constant, K, at 298 K for each of the following reactions:



$\Delta G = 0 = \Delta G^\circ + RT \ln K$   
 $\Delta G^\circ = (-497.9 \text{ kJ}) = - \left( \frac{0.008314 \text{ kJ}}{\text{mol K}} \right) 298 \text{ K} \ln K$   
 $\ln K = 200.96 \quad K = 1.89 \times 10^{87}$

19.78 Consider the following reaction:



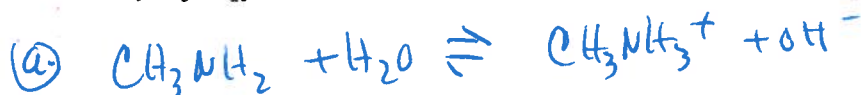
Using data in Appendix C, calculate the equilibrium pressure of CO<sub>2</sub> in the system at (a) 120°C and (b) 480°C.

$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

$\Delta G^\circ = 88.3 \text{ kJ} + (393 \text{ K})(-0.1513) = 28.8 \text{ kJ} = - \left( \frac{0.008314 \text{ kJ}}{\text{mol K}} \right) 298 \text{ K} \ln K$

$\ln K = -8.53 \quad K = P_{\text{CO}_2} = 1.48 \times 10^{-4} \text{ atm}$

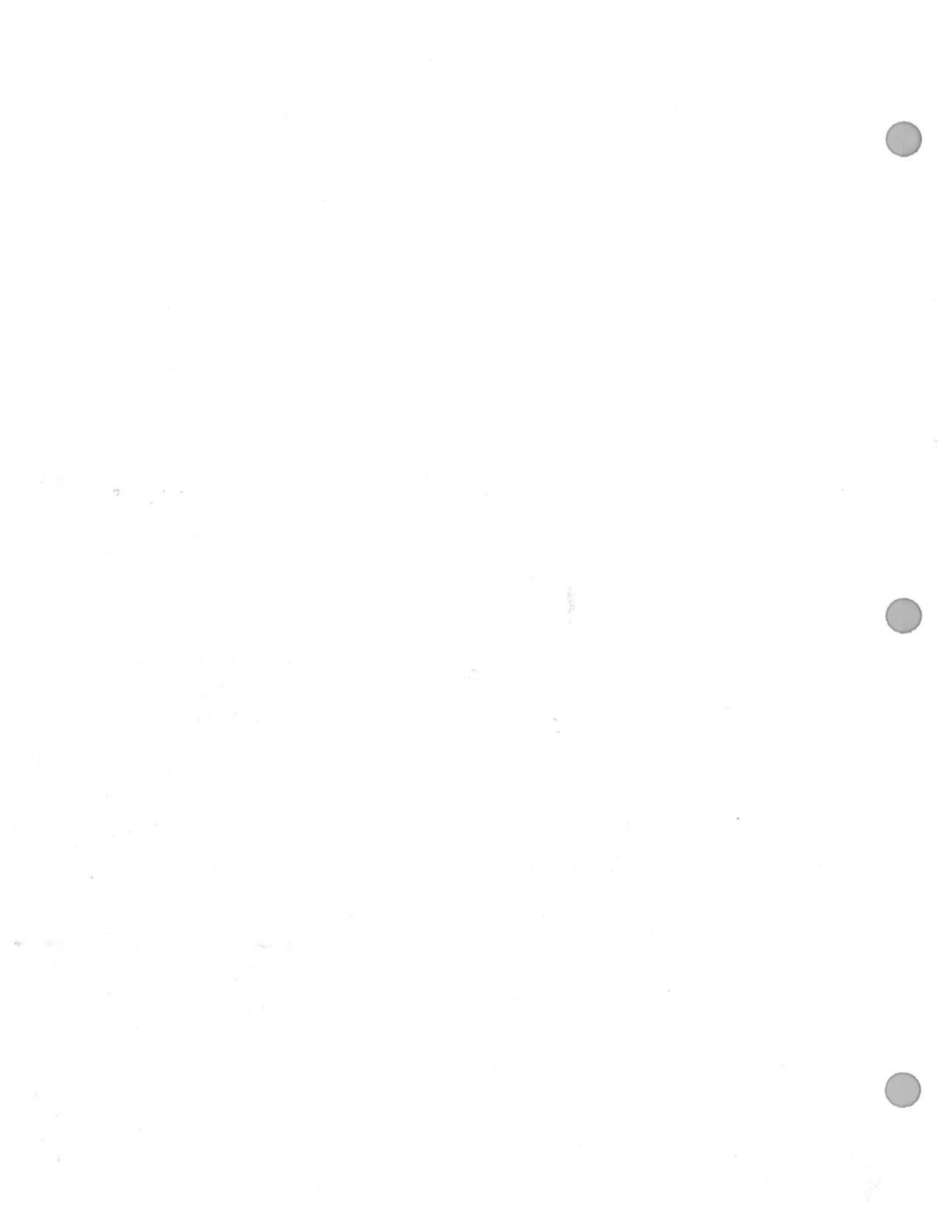
19.80 The K<sub>b</sub> for methylamine (CH<sub>3</sub>NH<sub>2</sub>) at 25°C is given in Appendix D. (a) Write the chemical equation for the equilibrium that corresponds to K<sub>b</sub>. (b) By using the value of K<sub>b</sub>, calculate  $\Delta G^\circ$  for the equilibrium in part (a). (c) What is the value of  $\Delta G$  at equilibrium? (d) What is the value of  $\Delta G$  when [H<sup>+</sup>] = 1.5 × 10<sup>-8</sup> M, [CH<sub>3</sub>NH<sub>3</sub><sup>+</sup>] = 5.5 × 10<sup>-4</sup> M, and [CH<sub>3</sub>NH<sub>2</sub>] = 0.120 M?



(b)  $\Delta G^\circ = -RT \ln K_b = - \left( \frac{0.008314 \text{ kJ}}{\text{mol K}} \right) (298 \text{ K}) \ln (4.4 \times 10^{-4}) = 19.1 \text{ kJ}$

(c) zero (d)  $\Delta G = \Delta G^\circ + RT \ln Q = 19.148 + \left( \frac{0.008314}{\text{mol K}} \right) (298) \ln \left( \frac{5.5 \times 10^{-4}}{1.5 \times 10^{-8}} \right)$

(d)  $\Delta G = -19.1 \text{ kJ}$



## AP Chemistry Notes - Chapter 19 - Thermodynamics

def. **THERMODYNAMICS** = the study of the interconversion of heat and other forms of energy

**First Law of Thermodynamics** - energy can be converted from one form to another, but it cannot be created or destroyed

Why study thermodynamics? The study of thermodynamics allows one to predict whether or not a reaction will occur under specified conditions.

def. **SPONTANEOUS REACTION** - a reaction is said to be spontaneous if it **does** occur under a certain set of conditions; spontaneous processes do not need an outside energy source to make them occur

*Examples of physical and chemical processes which are spontaneous:*

- A waterfall runs downhill.
- Sugar dissolving in coffee.
- Ice melting above 0°C (1 atm).
- A piece of sodium reacting w/ water to form NaOH and H<sub>2</sub>(g).
- Iron rusting when exposed to water.

**\*\* Notes:** Some of these spontaneous processes are fast and some are slow!

If a process is spontaneous in one direction, it is nonspontaneous in the other direction. All spontaneous processes are said to be irreversible under the given set of conditions.

(2) *Factors which determine the spontaneity of a reaction:*

- 1- Enthalpy (H) - most exothermic reactions tend to be spontaneous.
- 2- Entropy (S) - an increase in entropy favors spontaneous reactions

**Example:** Ice melting at room temperature. This is an endothermic process, yet it occurs spontaneously.

**ENTROPY (S)** = a measure of the randomness or disorder of a system; the larger the amount of disorder, the greater the entropy

- +ΔS = more randomness
- ΔS = less randomness

$$\Delta S = S_F - S_I$$

The following processes show an increase in entropy . . .

- a) melting of a solid  $S \rightarrow L$
- b) boiling or evaporating of a liquid  $L \rightarrow G$
- c) heating of a substance without changing its state  $S \rightarrow G$
- d) dissolving a solid to form an aqueous solution
- e) a reaction which produces more gas molecules than it consumes
- f) letting a gas expand into a larger volume *More disorder*

**SECOND LAW OF THERMODYNAMICS** = the entropy of the universe increases in a spontaneous process and remains unchanged in an equilibrium process (entropy is NOT conserved!)

\* For spontaneous (nonreversible) processes . . .  $\Delta S_{univ.} > 0$

\* For reversible processes . . .  $\Delta S_{univ.} = 0$

**Standard Entropy of a Reaction**,  $\Delta S^\circ_{rxn} = \Sigma S^\circ_{products} - \Sigma S^\circ_{reactants}$

The standard entropies ( $S^\circ$ ) are listed in App. C of your text. Notes concerning  $S^\circ$  values . . .

- \* all elements have entropy values (unlike enthalpies!)
- \*  $S^\circ_{gases} > S^\circ_{liquids} > S^\circ_{solids}$
- \* as MM increases,  $S^\circ$  increases
- \* as the number of atoms in compound increases,  $S^\circ$  also increases
- \* calculated entropy values are based upon a reference point of  $S=0$  for a perfect crystalline solid at 0 Kelvin. (Third Law of Thermodynamics says that the entropy of a perfect crystalline solid is zero at absolute zero.)

*App. C  
See Table*

Three types of motions associated which can increase entropy:

- A- translational motion = entire molecule moving
- B- vibrational motion = atoms within a molecule vibrating
- C - rotational motion = movement of molecules as if they were spinning like a top

*Overhead  
ppt*

**Gibbs Free Energy (G)** = the energy available to useful work

$-\Delta G$  means a process is spontaneous!

$+\Delta G$  means that a reaction is not spontaneous!

$\Delta G = 0$  means the system is at equilibrium

$$\Delta G = \Delta H - T\Delta S$$

**Standard Free Energy ( $\Delta G^\circ$ )** is the free-energy change for a reaction when it occurs under standard state conditions (298 K and 1 atm), when reactants in their standard states are converted to products in their standard states; the units are kJ

standard states . . . for gases = 1 atm  
liquids = pure  
solids = pure  
solutions = 1 M

$$\Delta G = \Delta H - T\Delta S$$

Effect of temperature on the spontaneity of a reaction:

| $\Delta H$ | $\Delta S$ | $\Delta G$ | <u>spontaneous rx?</u>               |
|------------|------------|------------|--------------------------------------|
| neg        | pos        | neg        | yes                                  |
| pos        | neg        | pos        | no                                   |
| neg        | neg        | ?          | yes at low temp's; no at high temp's |
| pos        | pos        | ?          | yes at high temp's; no at low temp's |

**Note:** For a reaction to be spontaneous, the  $\Delta H$  term must be smaller than the  $-T\Delta S$  term. If the  $\Delta H$  term is smaller, then the  $\Delta G$  is negative and the reaction is spontaneous!

**Standard free energy of formation ( $\Delta G^\circ_f$ )** = free energy change that occurs when 1 mole of the compound is synthesized from its elements in their standard states; the units are kJ/mol; the  $\Delta G^\circ_f$  of all free elements is zero (see app. C)

on Back

## Section 19.7: Relationship Between Free Energy and Equilibrium

**How to calculate  $\Delta G$  from  $\Delta G^\circ$ :**

Most chemical reactions occur under nonstandard conditions. Therefore we would have to calculate  $\Delta G$  in stead of  $\Delta G^\circ$ . Since tabulated values for free energy are all at standard conditions, we need a way to convert from  $\Delta G$  to and  $\Delta G^\circ$  visa-versa. The equation to complete this conversion is . . .

$$G = \Delta G^\circ + RT \ln Q$$

$$R = 8.314 \text{ J/mol K}$$

$$T = \text{absolute temperature (K)}$$

$$Q = \text{reaction quotient for the reaction; constant for a reversible reaction not at equilibrium}$$

Under standard conditions,  $\Delta G$  is equal to  $\Delta G^\circ$  because  $Q=1$  and  $\ln 1 = 0$ . If we don't have standard conditions, we must use  $\Delta G = \Delta G^\circ + RT \ln Q!$

**The Relationship Between K (equilibrium constant) and  $\Delta G^\circ$ :**

When a system is at equilibrium, we use the equation . . .

$$K = e^{-\Delta G^\circ/RT} \quad \text{OR} \quad \Delta G^\circ = -RT \ln K$$

At Equilibrium  $\Delta G = 0$

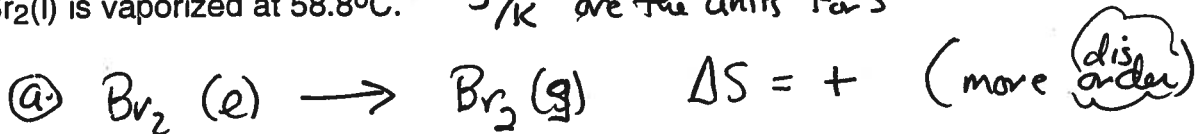
A  $K > 1$

B  $K = 1$

C  $K < 1$

Practice problems . . .

The normal boiling point of  $\text{Br}_2(\text{l})$  is  $58.8^\circ\text{C}$ , and its enthalpy of vaporization is  $\Delta H_{\text{vap}} = 29.6 \text{ kJ/mol}$ . (a) When  $\text{Br}_2(\text{l})$  boils at its normal boiling point, does its entropy increase or decrease? (b) Calculate the value of  $\Delta S$  when 1.00 mol of  $\text{Br}_2(\text{l})$  is vaporized at  $58.8^\circ\text{C}$ .  $\text{J/K}$  are the units for  $S$



$\Delta G = \Delta H - T\Delta S$   $\leftarrow$  0 at Equilib!

(b)  $\Delta S = \frac{\Delta H}{T} = \frac{29.6 \text{ kJ}}{\text{mol}} \cdot \frac{1.00 \text{ mol}}{332 \text{ K}} \cdot \frac{10^3 \text{ J}}{\text{kJ}} = \frac{89.2 \text{ J}}{\text{K}}$

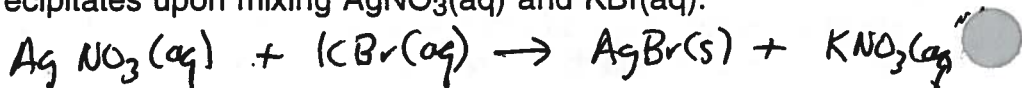
19.40 p. 839: Predict the sign of  $\Delta S$  for each of the following processes:

$\Delta S = -$  a) Molten iron solidifies.  $\text{L} \rightarrow \text{S}$

$\Delta S = -$  b)  $\text{LiCl}(\text{s})$  is formed from  $\text{Li}(\text{s})$  and  $\text{Cl}_2(\text{g})$ .  $\text{Li}(\text{s}) + \text{Cl}_2(\text{g}) \rightarrow \text{LiCl}(\text{s})$

$\Delta S = +$  c) Zinc metal dissolves in  $\text{HCl}$ , forming  $\text{ZnCl}_2(\text{aq})$  and  $\text{H}_2(\text{g})$ .  $\text{Zn} + \text{HCl} \rightarrow \text{ZnCl}_2(\text{aq}) + \text{H}_2$

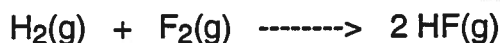
$\Delta S = -$  d) Silver bromide precipitates upon mixing  $\text{AgNO}_3(\text{aq})$  and  $\text{KBr}(\text{aq})$ .



19.53 a p. 840 Calculate the  $\Delta H^\circ$ ,  $\Delta S^\circ$ , and  $\Delta G^\circ$  at 298 K for the following reaction.

Also, show that  $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ .

Use Appendix C!



$\Delta H^\circ = 2(-268.61) - 0 + 0 = -537.22 \text{ kJ}$

$\Delta S^\circ = 2(173.51) - (130.58 + 202.7) = 13.74 \text{ J/K}$

$\Delta G^\circ = 2(-270.70) - [(0 + 0)] = -541.40 \text{ kJ}$

$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

$= -537.22 \text{ kJ} - (298 \text{ K}) \left( \frac{-0.01374 \text{ kJ}}{\text{K}} \right)$

$= -541.31 \text{ kJ}$

19.62 p. 840: A certain reaction is nonspontaneous at  $-25^{\circ}\text{C}$ . The entropy change for the reaction is  $95 \text{ J/K}$ . What can you conclude about the sign and the magnitude of  $\Delta H$ ?

☺  
+  
more disorder

$$\Delta G = \Delta H - T\Delta S$$

$$\Delta H = T\Delta S = 248 \text{ K} \left( \frac{95 \text{ J}}{\text{K}} \right)$$

$$\Delta H = 2.4 \times 10^4 \text{ J} \text{ or } 24 \text{ kJ}$$

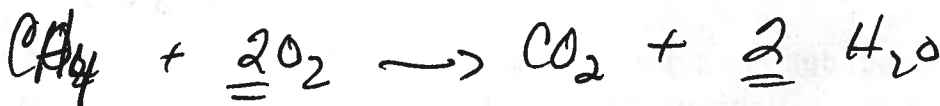
$$\Delta H \text{ must be } > 24 \text{ kJ}$$

Ends

similar to ...

19.69 on p. 841: Natural gas consists primarily of methane,  $\text{CH}_4$ . (a) How much heat is produced in the burning of a mole of methane under standard conditions if the reactants and products are brought to  $298 \text{ K}$  and  $\text{H}_2\text{O}(l)$  is formed? (b) What is the maximum amount of useful work that can be accomplished under standard conditions by this system?

Give this answer!



(a)  $-890.4 \text{ kJ/mol CH}_4 \text{ burned}$  (APP C)

(b)  $W_{\text{max}} = \Delta G^{\circ} = -817.9 \text{ kJ}$  (APP C)

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ} \quad \Delta S^{\circ} = -.243 \frac{\text{kJ}}{\text{K}} \text{ (APP C)}$$

19.73 on p. 841: Consider the reaction  $2 \text{NO}_2(\text{g}) \rightleftharpoons \text{N}_2\text{O}_4(\text{g})$ . (a) Calculate  $\Delta G^{\circ}$  at  $298 \text{ K}$ . (b) Calculate  $\Delta G$  at  $298 \text{ K}$  if the partial pressures of  $\text{NO}_2$  and  $\text{N}_2\text{O}_4$  are  $0.40 \text{ atm}$  and  $1.60 \text{ atm}$ , respectively.

P.25

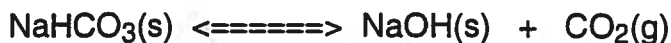
(a)  $\Delta G^{\circ} = \Delta G^{\circ} \text{ of } \text{N}_2\text{O}_4 - 2(\Delta G^{\circ} \text{ of } \text{NO}_2(\text{g})) = \text{spontaneous}$   
 $= 98.28 - 2(51.84) = -5.40 \text{ kJ}$

(b)  $\Delta G = \Delta G^{\circ} + RT \ln \left( \frac{\text{N}_2\text{O}_4}{\text{NO}_2^2} \right)$

$$= -5.40 \text{ kJ} + \frac{.008314 \text{ kJ}}{\text{mol K}} \left| \frac{298 \text{ K}}{1} \right| \ln \left( \frac{1.60}{.40^2} \right)$$

$$= .30 \text{ kJ}$$

19.26<sup>a</sup> on p. 84<sup>L</sup>: Write the equilibrium constant expression and calculate the value of the equilibrium constant for the following reaction at 298 K by using data from appendix C.



$$K_{\text{eq}} = [\text{CO}_2]$$

At Equilib  $\Delta G = 0$  so  $\Delta G^\circ = -RT \ln K$   $\ln K = -\frac{\Delta G^\circ}{RT}$

(a)  $\Delta G^\circ = (\Delta G^\circ \text{ of NaOH} + \Delta G^\circ \text{ of CO}_2) - \Delta G^\circ \text{ of NaHCO}_3$   
 $-379.5 \text{ kJ} + -394.4 \text{ kJ} - 857.8 \text{ kJ} = \boxed{+77.9 \text{ kJ}}$   
 Nonspont.

$$\ln K = -\frac{77.9 \text{ kJ}}{\left(\frac{8.314 \text{ J}}{\text{mol K}}\right)(298 \text{ K})} = -31.4 ; K = e^{-31.4} = \boxed{1.89 \times 10^{-14}}$$

**More practice!** For a given reaction  $\Delta H = 10.5 \text{ kJ}$  and  $\Delta S = 30 \text{ J/K}$ . Would this reaction be spontaneous at 25°C? If not, at what minimum temperature would it be spontaneous?

$$\Delta G = \overset{\text{Endo}}{\Delta H} - T \overset{\text{+}}{\Delta S}$$

$$= 10.5 \text{ kJ} - (298 \text{ K}) \left( \frac{.030 \text{ kJ}}{\text{K}} \right)$$

$$\Delta G = 1.56 \text{ Nonspontaneous}$$

Set  $\Delta G = 0$  to get min temp

$$0 = 10.5 \text{ kJ} - T \left( \frac{.030 \text{ kJ}}{\text{K}} \right)$$

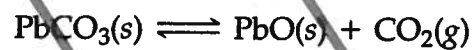
$$T \Rightarrow 350 \text{ K (or slightly greater)}$$



**More Practice!**



19.78 Consider the following reaction:



Using data in Appendix C, calculate the equilibrium pressure of  $\text{CO}_2$  in the system at (a)  $120^\circ\text{C}$  and (b)  $480^\circ\text{C}$ .

1971

Given the following data for graphite and diamond at 298K.

$$S^\circ(\text{diamond}) = 0.58 \text{ cal/mole deg}$$

$$S^\circ(\text{graphite}) = 1.37 \text{ cal/mole deg}$$

$$\Delta H_f^\circ \text{ CO}_2(\text{from graphite}) = -94.48 \text{ kilocalories/mole}$$

$$\Delta H_f^\circ \text{ CO}_2(\text{from diamond}) = -94.03 \text{ kilocalories/mole}$$

Consider the change:  $\text{C}(\text{graphite}) = \text{C}(\text{diamond})$  at 298K and 1 atmosphere.

- What are the values of  $\Delta S^\circ$  and  $\Delta H^\circ$  for the conversion of graphite to diamond.
- Perform a calculation to show whether it is thermodynamically feasible to produce diamond from graphite at 298K and 1 atmosphere.
- For the reaction, calculate the equilibrium constant  $K_{\text{eq}}$  at 298K

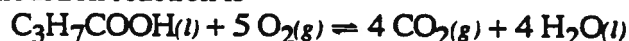


"Oool Now here's a nice one we built last fall."

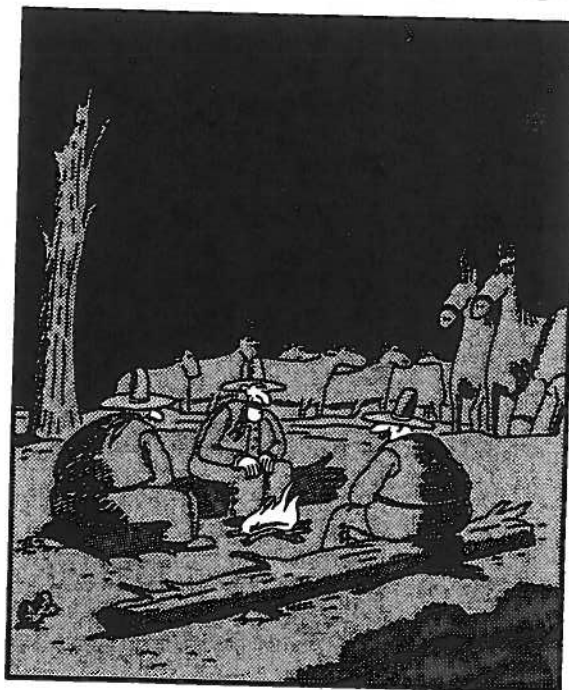
1984 B

| Substance                            | Standard Heat of Formation, $\Delta H_f^\circ$ ,<br>in $\text{kJ mol}^{-1}$ | Absolute Entropy, $S^\circ$ ,<br>in $\text{J mol}^{-1} \text{K}^{-1}$ |
|--------------------------------------|---|---|
| $\text{C}(s)$                        | 0.00  | 5.69  |
| $\text{CO}_2(g)$                     | -393.5  | 213.6   |
| $\text{H}_2(g)$                      | 0.00  | 130.6   |
| $\text{H}_2\text{O}(l)$              | -285.85   | 69.91   |
| $\text{O}_2(g)$                      | 0.00  | 205.0   |
| $\text{C}_3\text{H}_7\text{COOH}(l)$ | ?   | 226.3   |

The enthalpy change for the combustion of butyric acid at 25°C,  $\Delta H^\circ_{\text{comb}}$ , is -2,183.5 kilojoules per mole. The combustion reaction is



- From the above data, calculate the standard heat of formation,  $\Delta H_f^\circ$ , for butyric acid.
- Write a correctly balanced equation for the formation of butyric acid from its elements.
- Calculate the standard entropy change,  $\Delta S_f^\circ$ , for the formation of butyric acid at 25°C. The entropy change,  $\Delta S^\circ$ , for the combustion reaction above is  $-117.1 \text{ J K}^{-1}$  at 25°C.
- Calculate the standard free energy of formation,  $\Delta G_f^\circ$ , for butyric acid at 25°C.



"OK, I got one—do you say 'darn it' or 'dern it'?"

1977

Given the following data for graphite and diamond at 298K.

$$S^\circ(\text{diamond}) = 0.58 \text{ cal/mole deg}$$

$$S^\circ(\text{graphite}) = 1.37 \text{ cal/mole deg}$$

$$\Delta H_f^\circ \text{ CO}_2(\text{from graphite}) = -94.48 \text{ kilocalories/mole}$$

$\Delta H_f^\circ \text{ CO}_2(\text{from diamond}) = -94.03 \text{ kilocalories/mole}$   
 Consider the change:  $\text{C}(\text{graphite}) = \text{C}(\text{diamond})$  at 298K and 1 atmosphere.

- (a) What are the values of  $\Delta S^\circ$  and  $\Delta H^\circ$  for the conversion of graphite to diamond.  
 (b) Perform a calculation to show whether it is thermodynamically feasible to produce diamond from graphite at 298K and 1 atmosphere.  
 (c) For the reaction, calculate the equilibrium constant  $K_{\text{eq}}$  at 298K

**Answer:**

$$(a) \Delta S^\circ = S^\circ(\text{dia.}) - S^\circ(\text{graph.}) = (0.58 - 1.37) \text{ cal} \\ = -0.79 \text{ cal/K}$$



$$(b) \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -450 - (298)(-0.79) \text{ cal} \\ = -274.58 \text{ cal/mol}; \text{ a } \Delta G^\circ < 0 \text{ indicates feasible conditions}$$

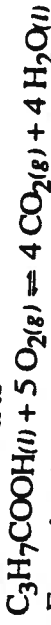
$$(c) K_{\text{eq}} = e^{-\Delta G^\circ/RT} = e^{-(-274.58)/(1.9872 \times 298)} = 1.437$$

1984 B

Answer Key  
4/13/98

| Substance                             | Standard Heat of Formation, $\Delta H_f^\circ$ , in kJ mol <sup>-1</sup> | Absolute Entropy, $S^\circ$ , in J mol <sup>-1</sup> K <sup>-1</sup> |
|---------------------------------------|--|--|
| C(s)                                  | 0.00   | 5.69   |
| CO <sub>2</sub> (g)                   | -393.5   | 213.6  |
| H <sub>2</sub> (g)                    | 0.00   | 130.6  |
| H <sub>2</sub> O(l)                   | -285.85  | 69.91  |
| O <sub>2</sub> (g)                    | 0.00   | 205.0  |
| C <sub>3</sub> H <sub>7</sub> COOH(l) | ?  | 226.3  |

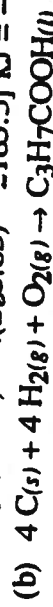
The enthalpy change for the combustion of butyric acid at 25°C,  $\Delta H^\circ_{\text{comb}}$  is -2,183.5 kilojoules per mole. The combustion reaction is



- (a) From the above data, calculate the standard heat of formation,  $\Delta H_f^\circ$ , for butyric acid.  
 (b) Write a correctly balanced equation for the formation of butyric acid from its elements.  
 (c) Calculate the standard entropy change,  $\Delta S_f^\circ$ , for the formation of butyric acid at 25°C. The entropy change,  $\Delta S^\circ$ , for the combustion reaction above is -117.1 J K<sup>-1</sup> at 25°C.  
 (d) Calculate the standard free energy of formation,  $\Delta G_f^\circ$ , for butyric acid at 25°C.

**Answer:**

$$(a) \Delta H = \sum \Delta H_f^\circ(\text{products}) - \sum \Delta H_f^\circ(\text{reactants}) \\ = [4(393.5) + 4(285.85) - 2183.5] \text{ kJ} = -533.8 \text{ kJ}$$



$$(c) \Delta S_f^\circ(\text{butyric acid}) = S^\circ(\text{butyric acid}) - [4 S^\circ(\text{C}) + 4 S^\circ(\text{H}_2) + S^\circ(\text{O}_2)]$$

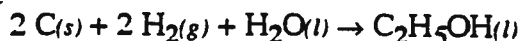
$$= 226.3 - [4(5.69) + 4(130.6) + 205] = -523.9 \text{ J/K}$$

$$(d) \Delta G_f^\circ = \Delta H_f^\circ - T\Delta S_f^\circ = 533.8 - (298)(-0.5239) \text{ kJ} \\ = -377.7 \text{ kJ}$$

1988 B

| Substance     | Enthalpy of Combustion, $\Delta H^\circ$ (kJ/mol) | Absolute Entropy, $S^\circ$ (J/mol-K) |
|---------------|---|---------------------------------------|
| $C_{(s)}$     | -393.5  | 5.740                                 |
| $H_{2(g)}$    | -285.8  | 130.6                                 |
| $C_2H_5OH(l)$ | -1366.7   | 160.7                                 |
| $H_2O(l)$     | --  | 69.91                                 |

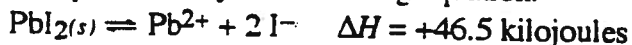
- (a) Write a separate, balanced chemical equation for the combustion of each of the following:  $C_{(s)}$ ,  $H_{2(g)}$ , and  $C_2H_5OH(l)$ . Consider the only products to be  $CO_2$  and/or  $H_2O(l)$ .
- (b) In principle, ethanol can be prepared by the following reaction:



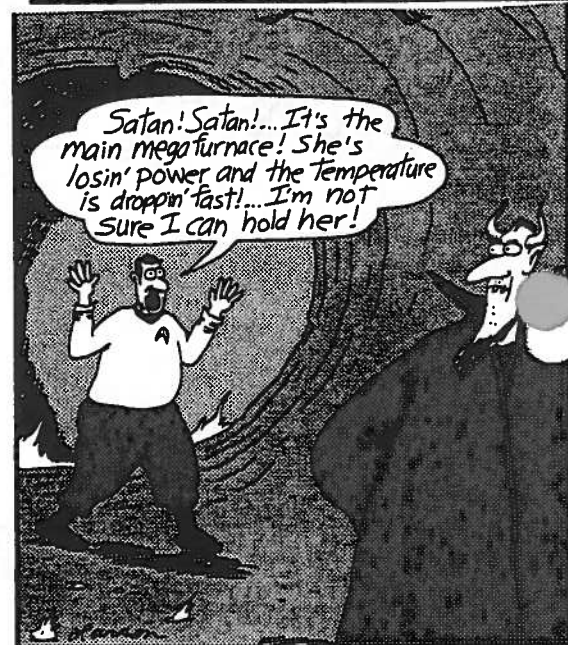
- Calculate the standard enthalpy change,  $\Delta H^\circ$ , for the preparation of ethanol, as shown in the reaction above.
- (c) Calculate the standard entropy change,  $\Delta S^\circ$ , for the reaction given in part (b).
- (d) Calculate the value of the equilibrium constant at  $25^\circ C$  for the reaction represented by the equation in part (b).

1995 D (repeated in the solid, liquid, solutions section)

Lead iodide is a dense, golden yellow, slightly soluble solid. At  $25^\circ C$ , lead iodide dissolves in water forming a system represented by the following equation.



- (a) How does the entropy of the system  $PbI_{2(s)} + H_2O(l)$  change as  $PbI_{2(s)}$  dissolves in water at  $25^\circ C$ ? Explain
- (b) If the temperature of the system were lowered from  $25^\circ C$  to  $15^\circ C$ , what would be the effect on the value of  $K_{sp}$ ? Explain.
- (c) If additional solid  $PbI_2$  were added to the system at equilibrium, what would be the effect on the concentration of  $I^-$  in the solution? Explain.
- (d) At equilibrium,  $\Delta G = 0$ . What is the initial effect on the value of  $\Delta G$  of adding a small amount of  $Pb(NO_3)_2$  to the system at equilibrium? Explain.



Scotty in hell

| Substance     | Enthalpy of Combustion, $\Delta H^\circ$ (kJ/mol) | Absolute Entropy, $S^\circ$ (J/mol-K) |
|---------------|---|---------------------------------------|
| $C(s)$        | -393.5  | 5.740                                 |
| $H_2(g)$      | -285.8  | 130.6                                 |
| $C_2H_5OH(l)$ | 1366.7  | 160.7                                 |
| $H_2O(l)$     | --  | 69.91                                 |

(a) Write a separate, balanced chemical equation for the combustion of each of the following:  $C(s)$ ,  $H_2(g)$ , and  $C_2H_5OH(l)$ . Consider the only products to be  $CO_2$  and/or  $H_2O(l)$ .

(b) In principle, ethanol can be prepared by the following reaction:

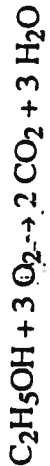
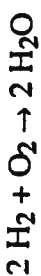


Calculate the standard enthalpy change,  $\Delta H^\circ$ , for the preparation of ethanol, as shown in the reaction above.

(c) Calculate the standard entropy change,  $\Delta S^\circ$ , for the reaction given in part (b).

(d) Calculate the value of the equilibrium constant at  $25^\circ C$  for the reaction represented by the equation in part (b).

**Answer:**



$\Delta H^\circ = 2(-393.5) = -787.0 \text{ kJ}$



$\Delta H^\circ = 2(-285.8) = -571.6 \text{ kJ}$



$\Delta H^\circ = -(-1366.7) = +1366.7 \text{ kJ}$



$\Delta H^\circ = +8.1 \text{ kJ}$

c)  $\Delta S = \sum S^\circ(\text{products}) - \sum S^\circ(\text{reactants})$

$= [160.7] - [11.5 + 261.2 + 69.9] \text{ J/mol.K}$

$= -181.9 \text{ J/mol.K}$

d)  $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = 8100 - (298)(-181.9) \text{ J}$

$= 62300 \text{ J}$

$K_{eq} = e^{-\Delta G^\circ/RT} = e^{-(62300/(8.3143)(298))} = 1.2 \times 10^{-11}$

**1995 D** (repeated in the solid, liquid, solutions section)

Lead iodide is a dense, golden yellow, slightly soluble solid. At  $25^\circ C$ , lead iodide dissolves in water forming a system represented by the following equation.



(a) How does the entropy of the system  $PbI_2(s)$  +  $H_2O(l)$  change as  $PbI_2(s)$  dissolves in water at  $25^\circ C$ ? Explain

(b) If the temperature of the system were lowered from  $25^\circ C$  to  $15^\circ C$ , what would be the effect on the value of  $K_{sp}$ ? Explain.

(c) If additional solid  $PbI_2$  were added to the system at equilibrium, what would be the effect on the concentration of  $I^-$  in the solution? Explain.

(d) At equilibrium,  $\Delta G = 0$ . What is the initial effect on the value of  $\Delta G$  of adding a small amount of  $Pb(NO_3)_2$  to the system at equilibrium? Explain.

**Answer: 1995 D**

(a) Entropy increases. At the same temperature, liquids and solids have a much lower entropy than do aqueous ions. Ions in solutions have much greater "degrees of freedom and randomness".

(b)  $K_{sp}$  value decreases.  $K_{sp} = [Pb^{2+}][I^-]^2$ . As the temperature is decreased, the rate of the forward (endothermic) reaction decreases resulting in a net decrease in ion concentration which produces a smaller  $K_{sp}$  value.

(c) No effect. The addition of more solid  $PbI_2$  does not change the concentration of the  $PbI_2$  which is a constant (at constant temperature), therefore, neither the rate of the forward nor reverse reaction is affected and the concentration of iodide ions remains the same.

(d)  $\Delta G$  increases. Increasing the concentration of  $Pb^{2+}$  ions causes a spontaneous increase in the reverse reaction rate (a "shift left" according to LeChâtelier's Principle). A reverse reaction is spontaneous when the  $\Delta G > 0$ .

1988 B

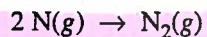
-285.8 kJ = 1

## 2003 AP<sup>®</sup> CHEMISTRY FREE-RESPONSE QUESTIONS

Answer EITHER Question 7 below OR Question 8 printed on page 14. Only one of these two questions will be graded. If you start both questions, be sure to cross out the question you do not want graded. The Section II score weighting for the question you choose is 15 percent.

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.

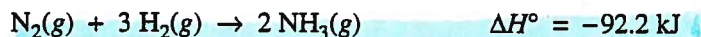


Using the table of average bond energies below, determine the enthalpy change,  $\Delta H$ , for the reaction.

$$\Delta H = \sum \text{bonds broken} - \sum \text{bonds formed}$$

| Bond  | Average Bond Energy<br>(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.

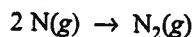
- (c) The value of  $\Delta G^\circ$  for the reaction represented in part (b) is negative at low temperatures but positive at high temperatures. Explain.
- (d) When  $\text{N}_2(g)$  and  $\text{H}_2(g)$  are placed in a sealed container at a low temperature, no measurable amount of  $\text{NH}_3(g)$  is produced. Explain.

AP CHEMISTRY  
2003 SCORING GUIDELINES

Question 7

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.

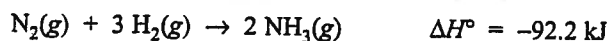


Using the table of average bond energies below, determine the enthalpy change,  $\Delta H$ , for the reaction.

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

|   |   |
|---|---|
| $\Delta H = -950 \text{ kJ}$<br>The reaction is exothermic because the chemical equation shows the formation of the N ≡ N bond. | 1 point for correct sign<br>1 point for magnitude |
|---|---|

(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.

|  |   |
|--|---|
| $\Delta S^\circ$ is negative. There are fewer moles of product gas (2 mol) compared to reactant gases (4 mol), so the reaction is becoming more ordered. | 1 point for correct sign<br>1 point for indicating fewer moles of products compared to reactants (in the gas phase) |
|--|---|

(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.

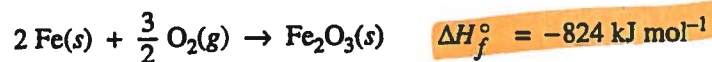
|  |  |
|--|--|
| $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$<br>$\Delta H^\circ$ and $\Delta S^\circ$ are negative. At low temperatures, the $T\Delta S^\circ$ term is smaller than $\Delta H^\circ$ , and $\Delta G^\circ$ is negative. At high temperatures, the $T\Delta S^\circ$ term is higher than $\Delta H^\circ$ , and $\Delta G^\circ$ is positive. | 1 point each for using $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ to explain the sign of $\Delta G^\circ$ at high and low temperatures. |
|--|--|

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

|  |   |
|--|---|
| Even though the reaction is spontaneous at low temperature, the reaction is very slow. The speed of a reaction depends on the fraction of colliding molecules with energy that exceeds the activation energy for the reaction. At low temperature, few reactant particles collide with an energy greater than the activation energy. | 1 point for indicating that the frequency of collision (or kinetic energy) of molecules is low at low temperature (thus the rate is slow)<br><br>1 point for indicating that at low temperature the kinetic energy will likely be too small to exceed the activation energy |
|--|---|

## 2004 AP<sup>®</sup> CHEMISTRY FREE-RESPONSE QUESTIONS

Answer EITHER Question 2 below OR Question 3 printed on page 8. Only one of these two questions will be graded. If you start both questions, be sure to cross out the question you do not want graded. The Section II score weighting for the question you choose is 20 percent.



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.

(a) Calculate the number of moles of each of the following before the reaction begins.

(i) Fe(s)

(ii) O<sub>2</sub>(g)

(b) 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.

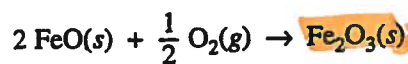
(c) Calculate the number of moles of Fe<sub>2</sub>O<sub>3</sub>(s) produced when the reaction proceeds to completion.

(d) The standard free energy of formation, ΔG<sub>f</sub><sup>°</sup>, of Fe<sub>2</sub>O<sub>3</sub>(s) is -740. kJ mol<sup>-1</sup> at 298 K.

(i) Calculate the standard entropy of formation, ΔS<sub>f</sub><sup>°</sup>, of Fe<sub>2</sub>O<sub>3</sub>(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, ΔH<sub>f</sub><sup>°</sup>, or the standard entropy of formation, ΔS<sub>f</sub><sup>°</sup>? Justify your answer.

The reaction represented below also produces iron(III) oxide. The value of ΔH<sup>°</sup> for the reaction is -280. kJ per mole of Fe<sub>2</sub>O<sub>3</sub>(s) formed.



(e) Calculate the standard enthalpy of formation, ΔH<sub>f</sub><sup>°</sup>, of FeO(s).



AP<sup>®</sup> CHEMISTRY  
2004 SCORING GUIDELINES

Question 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.

(a) Calculate the number of moles of each of the following before the reaction begins.

|                         |  |   |
|-------------------------|--|---|
| (i) Fe(s)               | $n_{\text{Fe}} = 75.0 \text{ g Fe} \times \left( \frac{1 \text{ mol Fe}}{55.85 \text{ g Fe}} \right) = 1.34 \text{ mol Fe}$  | 1 point for number of moles of Fe(s)              |
| (ii) O <sub>2</sub> (g) | $PV = nRT$ $n_{\text{O}_2} = \frac{PV}{RT} = \frac{2.66 \text{ atm} \times 11.5 \text{ L}}{0.0821 \frac{\text{L atm}}{\text{mol K}} \times 298 \text{ K}}$ $n_{\text{O}_2} = 1.25 \text{ mol O}_2$ | 1 point for number of moles of O <sub>2</sub> (g) |

(b) 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.

|  |   |
|--|---|
| $n_{\text{O}_2} \text{ reacting} = 1.34 \text{ mol Fe} \times \left( \frac{1.5 \text{ mol O}_2}{2 \text{ mol Fe}} \right)$ $= 1.01 \text{ mol O}_2$ <p>There is 1.25 mol O<sub>2</sub> initially, so there is an excess of O<sub>2</sub>, and Fe is the limiting reactant.</p>                     | 1 point for identifying limiting reactant |
| <p style="text-align: center;"><i>OR</i></p> $n_{\text{Fe}} \text{ reacting} = 1.25 \text{ mol O}_2 \times \left( \frac{2 \text{ mol Fe}}{1.5 \text{ mol O}_2} \right)$ $= 1.67 \text{ mol Fe}$ <p>There is 1.34 mol Fe initially, so there is not enough Fe, and Fe is the limiting reactant.</p> | 1 point for supporting calculation        |

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(c) Calculate the number of moles of Fe<sub>2</sub>O<sub>3</sub>(s) produced when the reaction proceeds to completion.

|  |  |
|--|--|
| $n_{\text{Fe}_2\text{O}_3} = 1.34 \text{ mol Fe} \times \left( \frac{1 \text{ mol Fe}_2\text{O}_3}{2 \text{ mol Fe}} \right) = 0.670 \text{ mol Fe}_2\text{O}_3$ | 1 point for number of moles of Fe <sub>2</sub> O <sub>3</sub> produced |
|--|--|

(d) The standard free energy of formation, ΔG<sub>f</sub><sup>°</sup>, of Fe<sub>2</sub>O<sub>3</sub>(s) is -740. kJ mol<sup>-1</sup> at 298 K.

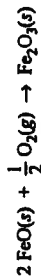
(i) Calculate the standard entropy of formation, ΔS<sub>f</sub><sup>°</sup>, of Fe<sub>2</sub>O<sub>3</sub>(s) at 298 K. Include units with your answer.

|   |  |
|---|--|
| $\Delta G_f^\circ = \Delta H_f^\circ - T \Delta S_f^\circ$ $-740. \text{ kJ mol}^{-1} = -824 \text{ kJ mol}^{-1} - (298 \text{ K}) \Delta S_f^\circ$ $+84 \text{ kJ mol}^{-1} = -(298 \text{ K}) \Delta S_f^\circ$ $\Delta S_f^\circ = \frac{+84 \text{ kJ mol}^{-1}}{-298 \text{ K}} = -0.28 \text{ kJ mol}^{-1} \text{ K}^{-1}$ | 1 point for calculation of ΔS <sub>f</sub> <sup>°</sup><br>1 point for correct units |
|---|--|

(ii) Which is more responsible for the spontaneity of the formation reaction at 298 K, the standard enthalpy of formation, ΔH<sub>f</sub><sup>°</sup>, or the standard entropy of formation, ΔS<sub>f</sub><sup>°</sup>? Justify your answer.

|  |  |
|--|--|
| <p>ΔH<sub>f</sub><sup>°</sup> is the more important factor. The reaction is exothermic, which favors spontaneity. ΔS<sub>f</sub><sup>°</sup> is negative, which means the system becomes more ordered as the reaction proceeds. Greater order will not increase the spontaneity of the reaction.</p> | 1 point for indicating that ΔH <sub>f</sub> <sup>°</sup> is responsible and for an explanation that addresses the signs of ΔH <sub>f</sub> <sup>°</sup> and ΔS <sub>f</sub> <sup>°</sup> |
|--|--|

The reaction represented below also produces iron(III) oxide. The value of ΔH<sup>°</sup> for the reaction is -280. kJ per mole of Fe<sub>2</sub>O<sub>3</sub>(s) formed.



(e) Calculate the standard enthalpy of formation, ΔH<sub>f</sub><sup>°</sup>, of FeO(s).

|   |  |
|---|--|
| $\Delta H_{\text{rxn}}^\circ = \sum \Delta H_f^\circ (\text{products}) - \sum \Delta H_f^\circ (\text{reactants})$ $\Delta H_{\text{rxn}}^\circ = \Delta H_f^\circ \text{Fe}_2\text{O}_3(s) - [2\Delta H_f^\circ \text{ of FeO}(s) + \frac{1}{2} \Delta H_f^\circ \text{ O}_2(g)]$ $-280. \text{ kJ mol}^{-1} = -824 \text{ kJ mol}^{-1} - [2\Delta H_f^\circ \text{ FeO}(s) + \frac{1}{2}(0)]$ $+544 \text{ kJ mol}^{-1} = -2\Delta H_f^\circ \text{ FeO}(s)$ $-272 \text{ kJ mol}^{-1} = \Delta H_f^\circ \text{ FeO}(s)$ | 1 point for correct stoichiometry<br>1 point for correct calculation |
|---|--|

## 2005 AP<sup>®</sup> CHEMISTRY FREE-RESPONSE QUESTIONS (Form B)

Answer EITHER Question 7 below OR Question 8 printed on page 14. Only one of these two questions will be graded. If you start both questions, be sure to cross out the question you do not want graded. The Section II score weighting for the question you choose is 15 percent.

7. Answer the following questions about thermodynamics.

| Substance             | Combustion Reaction   | Enthalpy of Combustion,<br>$\Delta H_{comb}^{\circ}$ , at 298 K (kJ mol <sup>-1</sup> ) |
|-----------------------|---|---|
| H <sub>2</sub> (g)    | H <sub>2</sub> (g) + $\frac{1}{2}$ O <sub>2</sub> (g) → H <sub>2</sub> O(l) | -290  |
| C(s)                  | C(s) + O <sub>2</sub> (g) → CO <sub>2</sub> (g)                             | -390  |
| CH <sub>3</sub> OH(l) |   | -730  |

- (a) In the empty box in the table above, write a balanced chemical equation for the complete combustion of one mole of CH<sub>3</sub>OH(l). Assume products are in their standard states at 298 K. Coefficients do not need to be whole numbers.
- (b) On the basis of your answer to part (a) and the information in the table, determine the enthalpy change for the reaction C(s) + H<sub>2</sub>(g) + H<sub>2</sub>O(l) → CH<sub>3</sub>OH(l).
- (c) Write the balanced chemical equation that shows the reaction that is used to determine the enthalpy of formation for one mole of CH<sub>3</sub>OH(l).
- (d) Predict the sign of  $\Delta S^{\circ}$  for the combustion of H<sub>2</sub>(g). Explain your reasoning.
- (e) On the basis of bond energies, explain why the combustion of H<sub>2</sub>(g) is exothermic.

Question 7

Answer the following questions about thermodynamics.

| Substance             | Combustion Reaction  | Enthalpy of Combustion,<br>$\Delta H^\circ_{\text{comb}}$ , at 298 K (kJ mol <sup>-1</sup> ) |
|-----------------------|--|--|
| H <sub>2</sub> (g)    | $\text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{l})$ | -290   |
| C(s)                  | $\text{C}(\text{s}) + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})$                      | -390   |
| CH <sub>3</sub> OH(l) |  | -730   |

- (a) In the empty box in the table above, write a balanced chemical equation for the complete combustion of one mole of CH<sub>3</sub>OH(l). Assume products are in their standard states at 298 K. Coefficients do not need to be in whole numbers.

|  |  |
|--|--|
| $\text{CH}_3\text{OH}(\text{l}) + \frac{3}{2} \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2 \text{H}_2\text{O}(\text{l})$ | One point is earned for the correct products.<br>One point is earned for balancing the equation. |
|--|--|

- (b) On the basis of your answer to part (a) and the information in the table, determine the enthalpy change for the reaction  $\text{C}(\text{s}) + \text{H}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{CH}_3\text{OH}(\text{l})$ .

|  |  |  |
|--|--|--|
| <p>Adding the following three equations,</p> $\text{C}(\text{s}) + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})$ $\text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{l})$ $\text{CO}_2(\text{g}) + 2 \text{H}_2\text{O}(\text{l}) \rightarrow \text{CH}_3\text{OH}(\text{l}) + \frac{3}{2} \text{O}_2(\text{g})$ <p>yields this equation: <math>\text{C}(\text{s}) + \text{H}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{CH}_3\text{OH}(\text{l})</math></p> | <p>-390 kJ mol<sup>-1</sup></p> <p>-290 kJ mol<sup>-1</sup></p> <p>+730 kJ mol<sup>-1</sup></p> <p>+50 kJ mol<sup>-1</sup></p> | <p>One point is earned for the correct equations.</p> <p>One point is earned for the correct value of <math>\Delta H^\circ</math>.</p> |
|--|--|--|

- (c) Write the balanced chemical equation that shows the reaction that is used to determine the enthalpy of formation for one mole of CH<sub>3</sub>OH(l).

|   |   |
|---|---|
| $\text{C}(\text{s}) + 2 \text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{CH}_3\text{OH}(\text{l})$ | One point is earned for the correct equation. |
|---|---|

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AP<sup>®</sup> CHEMISTRY  
2005 SCORING GUIDELINES (Form B)  
Question 7 (continued)

- (d) Predict the sign of  $\Delta S^\circ$  for the combustion of H<sub>2</sub>(g). Explain your reasoning.

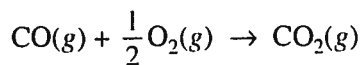
|  |   |
|--|---|
| <p><math>\Delta S^\circ</math> for the combustion of H<sub>2</sub>(g) is negative. Both reactants are in the gas phase and the product is in the liquid phase. The liquid phase is much more ordered than the gas phase, so the product is more ordered compared to the reactants, meaning that <math>\Delta S^\circ</math> is negative.</p> <p>(Note: There are fewer moles of products than reactants, which also favors a more ordered condition in the products, but the difference in phases is the more important factor.)</p> | <p>One point is earned for the correct sign of <math>\Delta S^\circ</math>.</p> <p>One point is earned for a correct explanation.</p> |
|--|---|

- (e) On the basis of bond energies, explain why the combustion of H<sub>2</sub>(g) is exothermic.

|  |   |
|--|---|
| <p>The combustion of H<sub>2</sub>(g) is exothermic (<math>\Delta H^\circ &lt; 0</math>) because more energy is released during the formation of two moles of O-H bonds than is required to break one mole of H-H bonds and one-half of a mole of O-O bonds.</p> | <p>One point is earned for the correct explanation.</p> |
|--|---|

**2006 AP<sup>®</sup> CHEMISTRY FREE-RESPONSE QUESTIONS**

Answer EITHER Question 2 below OR Question 3 printed on page 8. Only one of these two questions will be graded. If you start both questions, be sure to cross out the question you do not want graded. The Section II score weighting for the question you choose is 20 percent.



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

- (a) 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.

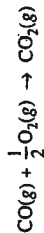


- (b) Determine the value of the standard entropy change,  $\Delta S_{rxn}^\circ$ , for the combustion of  $\text{CO}(g)$  at 298 K using the information in the following table.

| Substance        | $S_{298}^\circ$<br>( $\text{J mol}^{-1} \text{K}^{-1}$ ) |
|------------------|--|
| $\text{CO}(g)$   | 197.7  |
| $\text{CO}_2(g)$ | 213.7  |
| $\text{O}_2(g)$  | 205.1  |

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

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2006 SCORING GUIDELINES  
Question 2

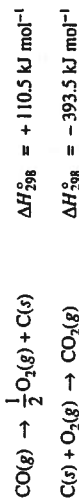


2. The combustion of carbon monoxide is represented by the equation above.

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



Reverse the first equation and add it to the second equation to obtain the third equation.



OR

$$\begin{aligned} \Delta H_{298}^\circ &= \Delta H_f^\circ \text{ of } \text{CO}_2(g) - \Delta H_f^\circ \text{ of } \text{CO}(g) \\ &= -393.5 \text{ kJ mol}^{-1} - (-110.5 \text{ kJ mol}^{-1}) = -283.0 \text{ kJ mol}^{-1} \end{aligned}$$

One point is earned for reversing the first equation.  
One point is earned for the correct answer (with sign).

OR

Two points are earned for determining  $\Delta H_{298}^\circ$  from the enthalpies of formation.  
(If sign is incorrect, only one point is earned.)

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2006 SCORING GUIDELINES  
Question 2 (continued)

$$\begin{aligned} \Delta S_{298}^\circ &= 213.7 \text{ J mol}^{-1} \text{ K}^{-1} - (197.7 \text{ J mol}^{-1} \text{ K}^{-1} + \frac{1}{2}(205.1 \text{ J mol}^{-1} \text{ K}^{-1})) \\ &= -86.5 \text{ J mol}^{-1} \text{ K}^{-1} \end{aligned}$$

One point is earned for taking one-half of  $S_{298}^\circ$  for  $\text{O}_2(g)$ .

One point is earned for the answer (with sign).

(c) Determine the standard free energy change,  $\Delta G_{298}^\circ$ , for the reaction at 298 K. Include units with your answer.

$$\begin{aligned} \Delta G_{298}^\circ &= \Delta H_{298}^\circ - T \Delta S_{298}^\circ \\ &= -283.0 \text{ kJ mol}^{-1} - (298 \text{ K})(-0.0865 \text{ kJ mol}^{-1} \text{ K}^{-1}) \\ \Delta G_{298}^\circ &= -257.2 \text{ kJ mol}^{-1} \end{aligned}$$

One point is earned for substituting the values from parts (a) and (b) into the equation.

One point is earned for the answer (with sign and units).

(d) Is the reaction spontaneous under standard conditions at 298 K? Justify your answer.

Yes, the reaction is spontaneous because the value of  $\Delta G_{298}^\circ$  for the reaction is negative ( $-257.2 \text{ kJ mol}^{-1}$ ).

One point is earned for an answer with justification (consistent with the answer in part (c)).

(e) Calculate the value of the equilibrium constant,  $K_{eq}$ , for the reaction at 298 K.

$$\begin{aligned} \Delta G_{298}^\circ &= -RT \ln K_{eq} \Rightarrow \frac{\Delta G_{298}^\circ}{-RT} = \ln K_{eq} \\ \frac{-257,200 \text{ J mol}^{-1}}{-(8.31 \text{ J mol}^{-1} \text{ K}^{-1})(298 \text{ K})} &= \ln K_{eq} \Rightarrow K_{eq} = 1.28 \times 10^5 \end{aligned}$$

One point is earned for correct substitution into the equation.

One point is earned for the answer.

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

| Substance        | $S_{298}^\circ$<br>(J mol <sup>-1</sup> K <sup>-1</sup> ) |
|------------------|---|
| $\text{CO}(g)$   | 197.7   |
| $\text{CO}_2(g)$ | 213.7   |
| $\text{O}_2(g)$  | 205.1   |

AP Chemistry  
Practice Exam - Thermodynamics

Name \_\_\_\_\_  
Date \_\_\_\_\_ Period \_\_\_\_\_

1. Solve the following problems in the spaces provided below.

$$\Delta H = -2448.5 \text{ kJ}$$

Use Hess' Law to calculate  $\Delta H$  for the following reaction:



Given:



2. Given the following information:

$$\Delta H_f \text{ MgCl}_2\text{(s)} = -641.8 \text{ kJ/mol}$$

$$\Delta H_f \text{ Mg}^{2+}\text{(aq)} = -462.0 \text{ kJ/mol}$$

$$\Delta H_f \text{ Cl}^-\text{(aq)} = -167.4 \text{ kJ/mol}$$

- A. Calculate  $\Delta H$  for the following reaction:  $\text{MgCl}_2\text{(s)} \rightarrow \text{Mg}^{2+}\text{(aq)} + 2 \text{ Cl}^-\text{(aq)}$

$$\Delta H = -155.0 \text{ kJ}$$

- B. If 3.17 g  $\text{MgCl}_2\text{(s)}$  (formula mass = 95.21) is dissolved in 250.0 g of water (S.H. = 4.184 J/g°C) in a coffee-cup calorimeter, what would the final temperature of the water be if the water were initially at 19.00°C?

$$= 23.9^\circ\text{C}$$

3. The heat of reaction for burning 1 mole of a certain compound X is known to be -477.7 kJ. The calorimeter constant of the bomb being used is  $2.5 \times 10^3 \text{ J/}^\circ\text{C}$  and the initial temperature of the water is 23.2°C.

- A. If 96.54 g of compound X (MM = 46) is burned in the bomb calorimeter containing 2000 ml of water (S.H. = 4.184 J/g°C) what will be the final Temp?

$$= 115.5^\circ\text{C}$$

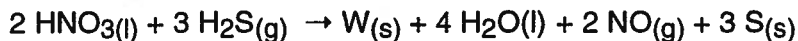
- B. How much water can be warmed from 23.2°C to 56.5°C when 172.0 g of the compound is burned in the bomb?

$$12,250 \text{ g or } 12,250 \text{ mL}$$

4. Which choice would definitely be non-spontaneous for the following changes in enthalpy ( $\Delta H$ ) and entropy ( $\Delta S$ )? (B)

- A.  $+\Delta H$  and  $+\Delta S$
- B.  $+\Delta H$  and  $-\Delta S$
- C.  $-\Delta H$  and  $+\Delta S$
- D.  $-\Delta H$  and  $-\Delta S$
- E.  $\Delta H = 0$  and  $+\Delta S$

5. The following chemical reaction occurs at  $25^\circ\text{C}$ :



You are given the following thermodynamic data:

| Species                        | $\Delta H^\circ_f$ (kJ/mol) | $\Delta G^\circ_f$ (kJ/mol) |
|--------------------------------|-----------------------------|-----------------------------|
| $\text{HNO}_3(\text{l})$       | -174.1                      | -80.8                       |
| $\text{H}_2\text{S}(\text{g})$ | -20.6                       | -33.6                       |
| $\text{H}_2\text{O}(\text{l})$ | -285.8                      | -237.2                      |
| $\text{NO}(\text{g})$          | 90.2                        | 86.6                        |

A. What is the value of the standard Gibbs Free Energy for the system represented above?  $\Delta G^\circ = -513.2 \frac{\text{kJ}}{\text{mol}}$

B. What is the value of the equilibrium constant for the system represented above?  $K_{\text{eq}} = 9.097 \times 10^{89}$

C. Calculate  $\Delta S^\circ$  at  $25^\circ\text{C}$ .  $\Delta S = -133 \frac{\text{J}}{\text{mol K}}$

6. A 50.0 g piece of metal at  $60.0^\circ\text{C}$  is placed in 200.0 g of water at  $22.0^\circ\text{C}$  contained in a coffee cup calorimeter. The metal and water come to the same temperature at  $32.5^\circ\text{C}$ .

A. How much heat did the metal give up to the water?  $8790 \text{ J} = q_{\text{water}}$

B. What is the specific heat of the metal?  $6.39 \frac{\text{J}}{\text{g}^\circ\text{C}}$

C. How many grams of the metal at  $80^\circ\text{C}$  would have to be used to heat half as much water (100.0g) to the same temperature?  $14.5 \text{ g metal}$

# Thermodynamic Quantities for Selected Substances at 298.15 K (25°C)

| Substance                          | $\Delta H_f^\circ$<br>(kJ/mol) | $\Delta G_f^\circ$<br>(kJ/mol) | $S^\circ$<br>(J/mol-K) | Substance                              | $\Delta H_f^\circ$<br>(kJ/mol) | $\Delta G_f^\circ$<br>(kJ/mol) | $S^\circ$<br>(J/mol-K) |
|------------------------------------|--------------------------------|--------------------------------|------------------------|--|--------------------------------|--------------------------------|------------------------|
| Chlorine                           |                                |                                |                        | Lead                                   |                                |                                |                        |
| Cl <sub>2</sub> (g)                | 121.7                          | 105.7                          | 165.2                  | Pb(s)                                  | 0                              | 0                              | 68.85                  |
| Cl <sup>-</sup> (aq)               | -167.2                         | -131.2                         | 56.5                   | PbBr <sub>2</sub> (s)                  | -277.4                         | -260.7                         | 161                    |
| Cl <sub>2</sub> (l)                | 0                              | 0                              | 222.96                 | PbCO <sub>3</sub> (s)                  | -699.1                         | -625.5                         | 131.0                  |
| HCl(aq)                            | -167.2                         | -131.2                         | 56.5                   | Pb(NO <sub>3</sub> ) <sub>2</sub> (aq) | -421.3                         | -246.9                         | 303.3                  |
| HCl(g)                             | -92.30                         | -95.27                         | 186.69                 | Pb(NO <sub>3</sub> ) <sub>2</sub> (s)  | -451.9                         | —                              | —                      |
| Chromium                           |                                |                                |                        | PbO(s)                                 | -217.3                         | -187.9                         | 68.70                  |
| Cr(g)                              | 397.5                          | 352.6                          | 174.2                  | Lithium                                |                                |                                |                        |
| Cr(s)                              | 0                              | 0                              | 23.6                   | Li(s)                                  | 159.3                          | 126.6                          | 138.8                  |
| Cr <sub>2</sub> O <sub>3</sub> (s) | -1139.7                        | -1058.1                        | 81.2                   | Li <sup>+</sup> (g)                    | 0                              | 0                              | 29.09                  |
| Cobalt                             |                                |                                |                        | Li <sup>+</sup> (g)                    | 685.7                          | 648.5                          | 133.0                  |
| Co(s)                              | 439                            | 393                            | 179                    | LiCl(s)                                | -408.3                         | -384.0                         | 59.30                  |
| Co(g)                              | 0                              | 0                              | 28.4                   | Magnesium                              |                                |                                |                        |
| Copper                             |                                |                                |                        | Mg(s)                                  | 147.1                          | 112.5                          | 148.6                  |
| Cu(s)                              | 338.4                          | 298.6                          | 166.3                  | Mg(s)                                  | 0                              | 0                              | 32.51                  |
| Cu <sub>2</sub> (s)                | 0                              | 0                              | 33.30                  | MgCl <sub>2</sub> (s)                  | -641.6                         | -592.1                         | 89.6                   |
| CuCl <sub>2</sub> (s)              | -205.9                         | -161.7                         | 108.1                  | MgO(s)                                 | -601.8                         | -569.6                         | 26.8                   |
| CuO(s)                             | -156.1                         | -128.3                         | 42.59                  | Mg(OH) <sub>2</sub> (s)                | -924.7                         | -833.7                         | 63.24                  |
| Cu <sub>2</sub> O(s)               | -170.7                         | -147.9                         | 92.36                  | Manganese                              |                                |                                |                        |
| Fluorine                           |                                |                                |                        | Mn(s)                                  | 280.7                          | 238.5                          | 173.6                  |
| F <sub>2</sub> (g)                 | 80.0                           | 61.9                           | 158.7                  | Mn(s)                                  | 0                              | 0                              | 32.0                   |
| F <sup>-</sup> (aq)                | -332.6                         | -278.8                         | -13.8                  | MnO(s)                                 | -385.2                         | -362.9                         | 59.7                   |
| F <sub>2</sub> (l)                 | 0                              | 0                              | 202.7                  | MnO <sub>2</sub> (s)                   | -519.6                         | -464.8                         | 53.14                  |
| HF(g)                              | -268.61                        | -270.70                        | 173.51                 | MnO <sub>2</sub> ·(aq)                 | -541.4                         | -447.2                         | 191.2                  |
| Hydrogen                           |                                |                                |                        | Mercury                                |                                |                                |                        |
| H <sub>2</sub> (g)                 | 0                              | 0                              | 130.58                 | Hg(s)                                  | 60.83                          | 31.76                          | 174.89                 |
| H <sup>+</sup> (aq)                | 0                              | 0                              | 0                      | Hg(l)                                  | 0                              | 0                              | 77.40                  |
| H <sup>+</sup> (g)                 | 1536.2                         | 1517.0                         | 108.9                  | Hg <sub>2</sub> Cl <sub>2</sub> (s)    | -230.1                         | -184.0                         | 144.5                  |
| H <sub>2</sub> (l)                 | 0                              | 0                              | 130.58                 | Hg <sub>2</sub> Cl <sub>2</sub> (s)    | -264.9                         | -210.5                         | 192.5                  |
| Iodine                             |                                |                                |                        | Nickel                                 |                                |                                |                        |
| I <sub>2</sub> (g)                 | 106.60                         | 70.16                          | 180.66                 | Ni(s)                                  | 429.7                          | 384.5                          | 182.1                  |
| I <sup>-</sup> (aq)                | -55.19                         | -51.57                         | 111.3                  | Ni(s)                                  | 0                              | 0                              | 29.9                   |
| I <sub>2</sub> (l)                 | 62.25                          | 19.37                          | 260.57                 | NiCl <sub>2</sub> (s)                  | -305.3                         | -259.0                         | 97.65                  |
| I <sub>2</sub> (s)                 | 0                              | 0                              | 116.73                 | NiO(s)                                 | -239.7                         | -211.7                         | 37.99                  |
| HI(g)                              | 25.94                          | 1.30                           | 206.3                  | Nitrogen                               |                                |                                |                        |
| Iron                               |                                |                                |                        | N(g)                                   | 472.7                          | 455.5                          | 153.3                  |
| Fe(s)                              | 415.5                          | 369.8                          | 180.5                  | N <sub>2</sub> (g)                     | 0                              | 0                              | 191.50                 |
| Fe(s)                              | 0                              | 0                              | 27.15                  | N <sub>2</sub> H <sub>4</sub> (g)      | -80.29                         | -26.50                         | 111.3                  |
| Fe <sup>2+</sup> (aq)              | -87.86                         | -84.93                         | 113.4                  | NH <sub>3</sub> (aq)                   | -46.19                         | -16.66                         | 192.5                  |
| Fe <sup>3+</sup> (aq)              | -47.69                         | -10.54                         | 293.3                  | NH <sub>3</sub> (g)                    | -132.5                         | -79.31                         | 113.4                  |
| FeCl <sub>3</sub> (s)              | -341.8                         | -302.3                         | 117.9                  | NH <sub>4</sub> <sup>+</sup> (aq)      | 95.40                          | 159.4                          | 238.5                  |
| FeCl <sub>3</sub> (s)              | -400                           | -334                           | 142.3                  | NH <sub>4</sub> Cl(s)                  | 0                              | 0                              | —                      |
| FeO(s)                             | -271.9                         | -255.2                         | 60.75                  | NH <sub>4</sub> Cl(s)                  | -314.4                         | -203.0                         | 94.6                   |
| Fe <sub>2</sub> O <sub>3</sub> (s) | -822.16                        | -740.98                        | 89.96                  | NH <sub>4</sub> NO <sub>3</sub> (s)    | -365.6                         | -184.0                         | 151                    |
| Fe <sub>3</sub> O <sub>4</sub> (s) | -1117.1                        | -1014.2                        | 146.4                  | NO(g)                                  | 90.37                          | 86.71                          | 210.62                 |
| FeS <sub>2</sub> (s)               | -171.5                         | -160.1                         | 52.92                  |  |                                |                                |                        |

| Substance                          | $\Delta H_f^\circ$<br>(kJ/mol) | $\Delta G_f^\circ$<br>(kJ/mol) | $S^\circ$<br>(J/mol-K) | Substance   | $\Delta H_f^\circ$<br>(kJ/mol) | $\Delta G_f^\circ$<br>(kJ/mol) | $S^\circ$<br>(J/mol-K) |
|------------------------------------|--------------------------------|--------------------------------|------------------------|---|--------------------------------|--------------------------------|------------------------|
| Aluminum                           |                                |                                |                        | Carbon  |                                |                                |                        |
| Al(s)                              | 0                              | 0                              | 28.32                  | C(s)  | 718.4                          | 672.9                          | 158.0                  |
| AlCl <sub>3</sub> (s)              | -705.6                         | -630.0                         | 109.3                  | C(s, diamond)                                     | 1.88                           | 2.84                           | 2.43                   |
| Al <sub>2</sub> O <sub>3</sub> (s) | -1669.8                        | -1576.5                        | 51.00                  | C(s, graphite)                                    | 0                              | 0                              | 5.69                   |
| Barium                             |                                |                                |                        | CCl <sub>4</sub> (g)                              | -106.7                         | -64.0                          | 309.4                  |
| Ba(s)                              | 0                              | 0                              | 63.2                   | CCl <sub>4</sub> (l)                              | -139.3                         | -68.6                          | 214.4                  |
| BaCO <sub>3</sub> (s)              | -1216.3                        | -1137.6                        | 112.1                  | CF <sub>4</sub> (g)                               | -679.9                         | -635.1                         | 262.3                  |
| BaO(s)                             | -553.5                         | -525.1                         | 70.42                  | CH <sub>4</sub> (g)                               | -74.8                          | -50.8                          | 186.3                  |
| Beryllium                          |                                |                                |                        | C <sub>2</sub> H <sub>2</sub> (g)                 | 226.7                          | 209.2                          | 200.8                  |
| Be(s)                              | 0                              | 0                              | 9.44                   | C <sub>2</sub> H <sub>4</sub> (g)                 | 52.30                          | 68.11                          | 219.4                  |
| BeO(s)                             | -608.4                         | -579.1                         | 13.77                  | C <sub>2</sub> H <sub>6</sub> (g)                 | -84.68                         | -32.89                         | 229.5                  |
| Be(OH) <sub>2</sub> (s)            | -905.8                         | -817.9                         | 50.21                  | C <sub>3</sub> H <sub>8</sub> (g)                 | -103.85                        | -23.47                         | 269.9                  |
| Bromine                            |                                |                                |                        | C <sub>3</sub> H <sub>10</sub> (g)                | -124.73                        | -15.71                         | 310.0                  |
| Br(s)                              | 111.8                          | 82.38                          | 174.9                  | C <sub>3</sub> H <sub>10</sub> (l)                | -147.6                         | -15.0                          | 231.0                  |
| Br <sup>-</sup> (aq)               | -120.9                         | -102.8                         | 80.71                  | C <sub>4</sub> H <sub>10</sub> (g)                | 82.9                           | 129.7                          | 269.2                  |
| Br <sub>2</sub> (g)                | 30.71                          | 3.14                           | 245.3                  | C <sub>4</sub> H <sub>10</sub> (l)                | 49.0                           | 124.5                          | 172.8                  |
| Br <sub>2</sub> (l)                | 0                              | 0                              | 152.3                  | CH <sub>3</sub> OH(g)                             | -201.2                         | -161.9                         | 237.6                  |
| HBr(g)                             | -36.23                         | -53.22                         | 198.49                 | CH <sub>3</sub> OH(l)                             | -238.6                         | -166.23                        | 126.8                  |
| Calcium                            |                                |                                |                        | C <sub>2</sub> H <sub>5</sub> OH(g)               | -235.1                         | -168.5                         | 282.7                  |
| Ca(s)                              | 179.3                          | 145.5                          | 154.8                  | C <sub>2</sub> H <sub>5</sub> OH(l)               | -277.7                         | -174.76                        | 160.7                  |
| Ca(s)                              | 0                              | 0                              | 41.4                   | C <sub>6</sub> H <sub>12</sub> O <sub>6</sub> (s) | -1273.02                       | -910.4                         | 212.1                  |
| CaCO <sub>3</sub>                  |                                |                                |                        | CO(g)   | -110.5                         | -137.2                         | 197.9                  |
| (s, calcite)                       | -1207.1                        | -1128.76                       | 92.88                  | CO <sub>2</sub> (g)                               | -393.5                         | -394.4                         | 213.6                  |
| CaCl <sub>2</sub> (s)              | -795.8                         | -748.1                         | 104.6                  | HC <sub>2</sub> H <sub>3</sub> O <sub>2</sub> (l) | -487.0                         | -392.4                         | 159.8                  |
| CaF <sub>2</sub> (s)               | -1219.6                        | -1167.3                        | 68.87                  | Cesium  |                                |                                |                        |
| CaO(s)                             | -635.5                         | -604.17                        | 39.75                  | Cs(s)   | 76.50                          | 49.53                          | 175.6                  |
| Ca(OH) <sub>2</sub> (s)            | -986.2                         | -898.5                         | 83.4                   | Cs(g)   | 0                              | 0                              | 85.15                  |
| CaSO <sub>4</sub> (s)              | -1434.0                        | -1321.8                        | 106.7                  | CsCl(s)   | -442.8                         | -414.4                         | 101.2                  |



| Substance                           | $\Delta H_f^\circ$<br>(kJ/mol) | $\Delta G_f^\circ$<br>(kJ/mol) | $S^\circ$<br>(J/mol-K) | Substance                           | $\Delta H_f^\circ$<br>(kJ/mol) | $\Delta G_f^\circ$<br>(kJ/mol) | $S^\circ$<br>(J/mol-K) |
|-------------------------------------|--------------------------------|--------------------------------|------------------------|-------------------------------------|--------------------------------|--------------------------------|------------------------|
| NO <sub>2</sub> (g)                 | 33.84                          | 51.84                          | 240.45                 | Scandium                            |                                |                                |                        |
| N <sub>2</sub> O(g)                 | 81.6                           | 103.59                         | 220.0                  | Sc(g)                               | 377.8                          | 336.1                          | 174.7                  |
| N <sub>2</sub> O <sub>4</sub> (g)   | 9.66                           | 98.28                          | 304.3                  | Sc(s)                               | 0                              | 0                              | 34.6                   |
| NOCl(g)                             | 52.6                           | 66.3                           | 264                    | Selenium                            |                                |                                |                        |
| HNO <sub>3</sub> (aq)               | -206.6                         | -110.5                         | 146                    | H <sub>2</sub> Se(g)                | 29.7                           | 15.9                           | 219.0                  |
| HNO <sub>3</sub> (g)                | -134.3                         | -73.94                         | 266.4                  | Silicon                             |                                |                                |                        |
| Oxygen                              |                                |                                |                        | Si(g)                               | 368.2                          | 323.9                          | 167.8                  |
| O(g)                                | 247.5                          | 230.1                          | 161.0                  | Si(s)                               | 0                              | 0                              | 18.7                   |
| O <sub>2</sub> (g)                  | 0                              | 0                              | 205.0                  | SiC(s)                              | -73.22                         | -70.85                         | 16.61                  |
| O <sub>3</sub> (g)                  | 142.3                          | 163.4                          | 237.6                  | SiCl <sub>4</sub> (l)               | -640.1                         | -572.8                         | 239.3                  |
| OH <sup>-</sup> (aq)                | -230.0                         | -157.3                         | -10.7                  | SiO <sub>2</sub> (s, quartz)        | -910.9                         | -856.5                         | 41.84                  |
| H <sub>2</sub> O(g)                 | -241.8                         | -228.61                        | 188.7                  | Silver                              |                                |                                |                        |
| H <sub>2</sub> O(l)                 | -285.85                        | -236.81                        | 69.96                  | Ag(s)                               | 0                              | 0                              | 42.55                  |
| H <sub>2</sub> O <sub>2</sub> (g)   | -136.10                        | -105.48                        | 232.9                  | Ag <sup>+</sup> (aq)                | 105.90                         | 77.11                          | 73.93                  |
| H <sub>2</sub> O <sub>2</sub> (l)   | -187.8                         | -120.4                         | 109.6                  | AgCl(s)                             | -127.0                         | -109.70                        | 96.11                  |
| Phosphorus                          |                                |                                |                        | Ag <sub>2</sub> O(s)                | -31.05                         | -11.20                         | 121.3                  |
| P(g)                                | 316.4                          | 280.0                          | 163.2                  | AgNO <sub>3</sub> (s)               | -124.4                         | -33.41                         | 140.9                  |
| P <sub>2</sub> (g)                  | 144.3                          | 103.7                          | 218.1                  | Sodium                              |                                |                                |                        |
| P <sub>4</sub> (g)                  | 58.9                           | 24.4                           | 280                    | Na(g)                               | 107.7                          | 77.3                           | 153.7                  |
| P <sub>4</sub> (s, red)             | -17.46                         | -12.03                         | 22.85                  | Na(s)                               | 0                              | 0                              | 51.45                  |
| P <sub>4</sub> (s, white)           | 0                              | 0                              | 41.08                  | Na <sup>+</sup> (aq)                | -240.1                         | -261.9                         | 59.0                   |
| PCl <sub>3</sub> (g)                | -288.07                        | -269.6                         | 311.7                  | Na <sup>+</sup> (g)                 | 609.3                          | 574.3                          | 148.0                  |
| PCl <sub>3</sub> (l)                | -319.6                         | -272.4                         | 217                    | NaBr(aq)                            | -360.6                         | -364.7                         | 141                    |
| PF <sub>3</sub> (g)                 | -1594.4                        | -1520.7                        | 300.8                  | NaBr(s)                             | -361.4                         | -349.3                         | 86.82                  |
| PH <sub>3</sub> (g)                 | 5.4                            | 13.4                           | 210.2                  | Na <sub>2</sub> CO <sub>3</sub> (s) | -1130.9                        | -1047.7                        | 136.0                  |
| P <sub>4</sub> O <sub>6</sub> (s)   | -1640.1                        | —                              | —                      | NaCl(aq)                            | -407.1                         | -393.0                         | 115.5                  |
| P <sub>4</sub> O <sub>10</sub> (s)  | -2940.1                        | -2675.2                        | 228.9                  | NaCl(g)                             | -181.4                         | -201.3                         | 229.8                  |
| POCl <sub>3</sub> (g)               | -542.2                         | -502.5                         | 325                    | NaCl(s)                             | -410.9                         | -384.0                         | 72.33                  |
| POCl <sub>3</sub> (l)               | -597.0                         | -520.9                         | 222                    | NaHCO <sub>3</sub> (s)              | -947.7                         | -851.8                         | 102.1                  |
| H <sub>3</sub> PO <sub>4</sub> (aq) | -1288.3                        | -1142.6                        | 158.2                  | NaNO <sub>2</sub> (aq)              | -446.2                         | -372.4                         | 207                    |
| Potassium                           |                                |                                |                        | NaNO <sub>3</sub> (s)               | -467.9                         | -367.0                         | 116.5                  |
| K(g)                                | 89.99                          | 61.17                          | 160.2                  | NaOH(aq)                            | -469.6                         | -419.2                         | 49.8                   |
| K(s)                                | 0                              | 0                              | 64.67                  | NaOH(s)                             | -425.6                         | -379.5                         | 64.46                  |
| KCl(s)                              | -435.9                         | -408.3                         | 82.7                   | Strontium                           |                                |                                |                        |
| KClO <sub>3</sub> (s)               | -391.2                         | -289.9                         | 143.0                  | SrO(s)                              | -592.0                         | -561.9                         | 54.9                   |
| KClO <sub>4</sub> (aq)              | -349.5                         | -284.9                         | 265.7                  | Sr(g)                               | 164.4                          | 110.0                          | 164.6                  |
| KNO <sub>3</sub> (s)                | -492.70                        | -393.13                        | 288.1                  | Sulfur                              |                                |                                |                        |
| K <sub>2</sub> O(s)                 | -363.2                         | -322.1                         | 94.14                  | S(s, rhombic)                       | 0                              | 0                              | 31.88                  |
| KO <sub>2</sub> (s)                 | -284.5                         | -240.6                         | 122.5                  | SO <sub>2</sub> (g)                 | -296.9                         | -300.4                         | 248.5                  |
| K <sub>2</sub> O <sub>2</sub> (s)   | -495.8                         | -429.8                         | 113.0                  | SO <sub>3</sub> (g)                 | -395.2                         | -370.4                         | 256.2                  |
| KOH(s)                              | -424.7                         | -378.9                         | 78.91                  | SO <sub>3</sub> <sup>2-</sup> (aq)  | -909.3                         | -744.5                         | 20.1                   |
| KOH(aq)                             | -482.4                         | -440.5                         | 91.6                   | SOCl <sub>2</sub> (l)               | -245.6                         | —                              | —                      |
| Rubidium                            |                                |                                |                        | Vanadium                            |                                |                                |                        |
| Rb(g)                               | 85.8                           | 55.8                           | 170.0                  | V(g)                                | 514.2                          | 453.1                          | 182.2                  |
| Rb(s)                               | 0                              | 0                              | 76.78                  | V(s)                                | 0                              | 0                              | 28.9                   |
| RbCl(s)                             | -430.5                         | -412.0                         | 92                     | Titanium                            |                                |                                |                        |
| RbClO <sub>3</sub> (s)              | -392.4                         | -292.0                         | 152                    | Ti(g)                               | 468                            | 422                            | 180.3                  |
|                                     |                                |                                |                        | Ti(s)                               | 0                              | 0                              | 30.76                  |
|                                     |                                |                                |                        | TiCl <sub>4</sub> (g)               | -763.2                         | -726.8                         | 354.9                  |
|                                     |                                |                                |                        | TiCl <sub>4</sub> (l)               | -804.2                         | -728.1                         | 221.9                  |
|                                     |                                |                                |                        | TiO <sub>2</sub> (s)                | -944.7                         | -889.4                         | 50.29                  |
|                                     |                                |                                |                        | Zinc                                |                                |                                |                        |
|                                     |                                |                                |                        | Zn(g)                               | 130.7                          | 95.2                           | 160.9                  |
|                                     |                                |                                |                        | Zn(s)                               | 0                              | 0                              | 41.63                  |
|                                     |                                |                                |                        | ZnCl <sub>2</sub> (s)               | -415.1                         | -369.4                         | 111.5                  |
|                                     |                                |                                |                        | ZnO(s)                              | -348.0                         | -318.2                         | 43.9                   |

