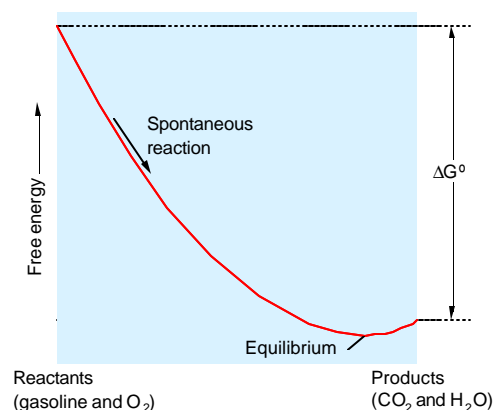


1. A spontaneous process is a chemical or physical change that occurs by itself without the continuing intervention of some outside force. Examples are a rock rolling down hill, iron rusting in moist air and ice cubes melting when left at room temperature. The reverse of these three processes are non-spontaneous processes.
2. The liquid benzene has higher entropy than solid benzene. In the solid, molecules occupy fixed locations within a crystalline lattice and do not move relative to each other. In the liquid phase, the molecules are free to move relative to each other. This results in greater disorder and therefore greater entropy than in the solid phase.
3. The Second Law states that for a spontaneous process, there must be an increase in the entropy of the universe.
4. For a spontaneous process, $\Delta S + \Delta S_{\text{surr}} > 0$. If we do not consider the possibility of useful work, $\Delta S_{\text{surr}} = -\Delta H/T$. Therefore, $\Delta S > \Delta H/T$ for a spontaneous process.
7. $G = H - TS$. For a process occurring at constant temperature, $\Delta G = \Delta H - T\Delta S$.
8. The standard free energy change for a reaction is the free energy change that accompanies the reaction where all reactants and products are in their standard states (pure substances at 1 bar of pressure). The standard free energy of formation, ΔG_f° is the free energy change for a reaction involving the formation of one mole of a substance in its standard state from its elements in their reference forms and standard states
13. As a spontaneous reaction occurs, the free energy of the system decreases until the reaction reaches a state of equilibrium. At equilibrium, the system has its minimum free energy and the reaction has no driving force in either direction, because reaction in either direction would require an increase in the free energy of the system.



15.

Sign of ΔH	Sign of ΔS	Sign of ΔG
negative	positive	negative at all temperatures
negative	negative	negative at low temperatures positive at high temperatures
positive	positive	positive at low temperatures negative at high temperatures
positive	negative	positive at all temperatures

16. We can estimate the temperature at which ΔG° goes from positive to negative, i.e., the temperature at which ΔG° equals zero. We solve for this temperature by setting ΔG° equal to zero in the equation

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ = 0$$

and solving for T. Note that the temperature will be in Kelvins.

$$T = \frac{\Delta H^\circ}{\Delta S^\circ}$$

17. a. False. Some spontaneous reactions are endothermic.
- b. False. Some spontaneous reactions like the conversion of diamond to graphite are so slow we could never hope to observe them.
- c. False. there are some spontaneous reactions in which the entropy of the system decreases, such as $2 \text{H}_2 (\text{g}) + \text{O}_2 (\text{g}) \rightarrow 2 \text{H}_2\text{O} (\text{l})$. The entropy of the universe, however, **must** increase.
- d. The total entropy of the system and its surroundings will always increase for a spontaneous process. One or the other may decrease, but must be accompanied by a larger increase in the other.
- e. False. Some spontaneous processes involve an increase in the energy of the system while some involve a decrease.

19. a. 2.0 mol of CO_2 (g) at 1 atm and 20°C has twice the entropy as 1.0 mol of CO_2 (g) at 1 atm and 20°C .
- b. The gaseous butane has the higher entropy.
- c. The CO_2 at the higher temperature (-80°C) has the higher entropy.
- d. The bromine vapor has the higher entropy.
22. The process is not spontaneous. It required the input of useful work to occur. Therefore, $\Delta G > 0$. The rubber band becomes warmer in the process, so heat was evolved and $\Delta H < 0$. Therefore, ΔS must be negative since $\Delta G = \Delta H - T \Delta S$. This is in agreement with the molecular picture of the rubber band where stretching leads to a more ordered state. Incidentally, if a stretched rubber band is heated, it will actually contract rather than expand. When the rubber band is heated, its entropy increases, and it goes to the more disordered, contracted state where its molecules are more randomly oriented.
25. Since the system loses or evolves 82 J of heat, $q = -82 \text{ J}$.

Since work is done on the system, $w = +29 \text{ J}$.

$$\Delta U = q + w = -82 \text{ J} + 29 \text{ J} = -53 \text{ J}$$

27. When 1.00 mol of water vaporizes at 100°C , it absorbs 40.66 kJ of energy in the form of heat ($\Delta H_{\text{vap}} = +40.66 \text{ kJ/mol}$). Therefore, $q = +40.66 \text{ kJ} = 40,660 \text{ J}$.

$w = -P_{\text{ext}} \Delta V$, so we must calculate subtract the volume of 1.00 mol of liquid water at 100°C from the volume of 1.00 mol of steam at 100°C .

$$V = \frac{nRT}{P} = \frac{(1.00 \text{ mol})(0.082058 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}})(373 \text{ K})}{1.00 \text{ atm}} = 30.6 \text{ L}$$

$$\Delta V = 30.6 \text{ L} - 0.018 \text{ L} \approx 30.6 \text{ L}$$

$$w = -1.00 \text{ atm} (30.6 \text{ L}) = -30.6 \text{ L} \cdot \text{atm} \times \frac{101.325 \text{ J}}{\text{L} \cdot \text{atm}} = -3.10 \times 10^3 \text{ J} = -3.10 \text{ kJ}$$

$$\Delta U = +40.66 \text{ kJ} + (-3.10 \text{ kJ}) = +37.56 \text{ kJ}$$

$$29. \Delta H = 1.20 \text{ mol} \times \frac{29.6 \text{ kJ}}{\text{mol}} = 35.5 \text{ kJ} = 35,500 \text{ J}$$

$$\text{At the normal boiling point, } \Delta S_{\text{vap}} = \frac{\Delta H_{\text{vap}}}{T} = \frac{35,500 \text{ J}}{334.4 \text{ K}} = 106 \frac{\text{J}}{\text{K}}$$

$$31. \Delta H = 1.00 \text{ mol} \times \frac{38.0 \text{ kJ}}{\text{mol}} = 38.0 \text{ kJ} = 3.80 \times 10^4 \text{ J}$$

$$\Delta S_{\text{vap}} = \frac{\Delta H_{\text{vap}}}{T} = \frac{38,000 \text{ J}}{298 \text{ K}} = 128 \frac{\text{J}}{\text{K}}$$

$$\Delta S \text{ for condensation} = -128 \frac{\text{J}}{\text{K}} \quad S(\text{g}) = 1.00 \text{ mol} \times 255 \frac{\text{J}}{\text{K} \cdot \text{mol}} = 255 \frac{\text{J}}{\text{K}}$$

$$-128 \frac{\text{J}}{\text{K}} = S(\text{l}) - S(\text{g}) = S(\text{l}) - 255 \frac{\text{J}}{\text{K}}$$

$$S(\text{l}) = 127. \frac{\text{J}}{\text{K}} \text{ for } 1.00 \text{ mol} = \frac{127 \frac{\text{J}}{\text{K} \cdot \text{mol}}}{1.00 \text{ mol}} = 127 \frac{\text{J}}{\text{K} \cdot \text{mol}}$$

33. a. $\Delta S^\circ < 0$ because 3 moles of gas are replaced by 1 mole of gas.

b. $\Delta S^\circ \approx 0$ because 2 moles of gas are replaced by 2 moles of gas.

c. $\Delta S^\circ > 0$ because 5 moles of gas are replaced by 6 moles of gas.

d. $\Delta S^\circ < 0$ because 2 moles of solid and 1 mole of gas are replaced by 2 moles of gas.

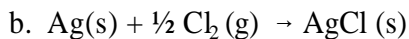
35. a. $2 \text{ Na (s)} + \text{Cl}_2 \text{ (g)} \rightarrow 2 \text{ NaCl (s)}$

$$\Delta S^\circ = 2 \text{ mol } (S^\circ (\text{NaCl (s)})) - [2 \text{ mol } (S^\circ (\text{Na (s)})) + 1 \text{ mol } (S^\circ (\text{Cl}_2 \text{ (g)}))]$$

$$\Delta S^\circ = 2 \text{ mol } (+72.12 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}) -$$

$$[2 \text{ mol } (+51.46 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}) + 1 \text{ mol } (+223.0 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})]$$

$$\Delta S^\circ = -181.7 \text{ J} \cdot \text{K}^{-1}$$

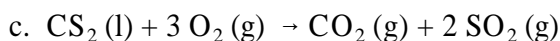


$$\Delta S^\circ = 1 \text{ mol } (S^\circ (\text{AgCl(s)})) - [\frac{1}{2} \text{ mol } (S^\circ (\text{Cl}_2(\text{g}))) + 1 \text{ mol } (S^\circ (\text{Ag(s)}))]$$

$$\Delta S^\circ = 1 \text{ mol } (+96.2 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})$$

$$- [\frac{1}{2} \text{ mol } (+223.0 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})] + 1 \text{ mol } (+42.55 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})]$$

$$\Delta S^\circ = -57.8 \text{ J} \cdot \text{K}^{-1}$$



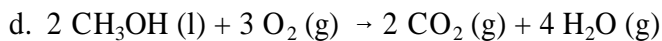
$$\Delta S^\circ = [1 \text{ mol } (S^\circ (\text{CO}_2(\text{g}))) + 2 \text{ mol } (S^\circ (\text{SO}_2(\text{g})))]$$

$$- [1 \text{ mol } (S^\circ (\text{CS}_2(\text{l}))) + 3 \text{ mol } (S^\circ (\text{O}_2(\text{g})))]$$

$$\Delta S^\circ = [1 \text{ mol } (+213.7 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}) + 2 \text{ mol } (+248.1 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})]$$

$$- [1 \text{ mol } (+151.3 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}) + 3 \text{ mol } (+205.0 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})]$$

$$\Delta S^\circ = -56.4 \text{ J} \cdot \text{K}^{-1}$$



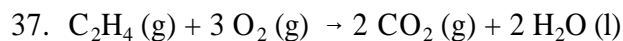
$$\Delta S^\circ = [2 \text{ mol } (S^\circ (\text{CO}_2(\text{g}))) + 4 \text{ mol } (S^\circ (\text{H}_2\text{O}(\text{g})))]$$

$$- [2 \text{ mol } (S^\circ (\text{CH}_3\text{OH}(\text{l}))) + 3 \text{ mol } (S^\circ (\text{O}_2(\text{g})))]$$

$$\Delta S^\circ = [2 \text{ mol } (+213.7 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}) + 4 \text{ mol } (+188.7 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})]$$

$$- [2 \text{ mol } (+126.8 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}) + 3 \text{ mol } (+205.0 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})]$$

$$\Delta S^\circ = +313.6 \text{ J} \cdot \text{K}^{-1}$$



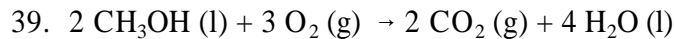
$$\Delta S^\circ = [2 \text{ mol } (S^\circ (\text{CO}_2(\text{g}))) + 2 \text{ mol } (S^\circ (\text{H}_2\text{O}(\text{l})))]$$

$$- [1 \text{ mol } (S^\circ (\text{C}_2\text{H}_4(\text{g}))) + 3 \text{ mol } (S^\circ (\text{O}_2(\text{g})))]$$

$$\Delta S^\circ = [2 \text{ mol } (+213.7 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}) + 2 \text{ mol } (+69.95 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})]$$

$$- [1 \text{ mol } (+219.2 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}) + 3 \text{ mol } (+205.0 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})]$$

$\Delta S^\circ = -255.9 \text{ J} \cdot \text{K}^{-1}$ We would expect ΔS° to be negative since 3 moles of gas are replace with 1 mole of gas and 2 moles of liquid.



$$\Delta H^\circ = [2 \text{ mol } (\Delta H_f^\circ (\text{CO}_2 (\text{g}))) + 4 \text{ mol } (\Delta H_f^\circ (\text{H}_2\text{O} (\text{l})))]$$

$$- [2 \text{ mol } (\Delta H_f^\circ (\text{CH}_3\text{OH} (\text{l}))) + 3 \text{ mol } (\Delta H_f^\circ (\text{O}_2 (\text{g})))]$$

$$\Delta H^\circ = [2 \text{ mol } (-393.5 \text{ kJ} \cdot \text{mol}^{-1}) + 4 \text{ mol } (-285.8 \text{ kJ} \cdot \text{mol}^{-1})]$$

$$- [2 \text{ mol } (-238.7 \text{ kJ} \cdot \text{mol}^{-1}) + 3 \text{ mol } (0 \text{ kJ} \cdot \text{mol}^{-1})]$$

$$\Delta H^\circ = -1452.8 \text{ kJ}$$

$$\Delta S^\circ = [2 \text{ mol } (S^\circ (\text{CO}_2 (\text{g}))) + 4 \text{ mol } (S^\circ (\text{H}_2\text{O} (\text{l})))]$$

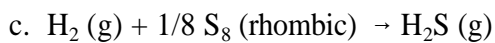
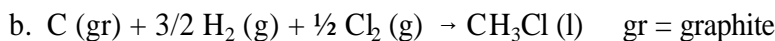
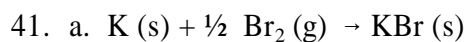
$$- [2 \text{ mol } (S^\circ (\text{CH}_3\text{OH} (\text{l}))) + 3 \text{ mol } (S^\circ (\text{O}_2 (\text{g})))]$$

$$\Delta S^\circ = [2 \text{ mol } (+213.7 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}) + 4 \text{ mol } (+69.95 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})]$$

$$- [2 \text{ mol } (+126.8 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}) + 3 \text{ mol } (+205.0 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})]$$

$$\Delta S^\circ = -161.4 \text{ J} \cdot \text{K}^{-1}$$

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ = -1,452,800 \text{ J} - 298 \text{ K } (-161.4 \text{ J} \cdot \text{K}^{-1}) = -1,404,700 \text{ J} = -1404.7 \text{ kJ}$$





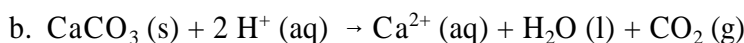
$$\Delta G^\circ = [2 \text{ mol } (\Delta G_f^\circ (\text{CO}_2(\text{g}))) + 2 \text{ mol } (\Delta G_f^\circ (\text{H}_2\text{O}(\text{l})))]$$

$$- [1 \text{ mol } (\Delta G_f^\circ (\text{C}_2\text{H}_4(\text{g}))) + 3 \text{ mol } (\Delta G_f^\circ (\text{O}_2(\text{g})))]$$

$$\Delta G^\circ = [2 \text{ mol } (-394.4 \text{ kJ} \cdot \text{mol}^{-1}) + 2 \text{ mol } (-237.1 \text{ kJ} \cdot \text{mol}^{-1})]$$

$$- [1 \text{ mol } (-68.39 \text{ kJ} \cdot \text{mol}^{-1}) + 3 \text{ mol } (0 \text{ kJ} \cdot \text{mol}^{-1})]$$

$$\Delta G^\circ = -1194.6 \text{ kJ}$$



$$\Delta G^\circ = [1 \text{ mol } (\Delta G_f^\circ (\text{CO}_2(\text{g}))) + 1 \text{ mol } (\Delta G_f^\circ (\text{H}_2\text{O}(\text{l}))) + 1 \text{ mol } (\Delta G_f^\circ (\text{Ca}^{2+}(\text{aq})))]$$

$$- [1 \text{ mol } (\Delta G_f^\circ (\text{CaCO}_3(\text{s}))) + 2 \text{ mol } (\Delta G_f^\circ (\text{H}^+(\text{aq})))]$$

$$\Delta G^\circ = [1 \text{ mol } (-394.4 \text{ kJ} \cdot \text{mol}^{-1}) + 1 \text{ mol } (-237.1 \text{ kJ} \cdot \text{mol}^{-1}) + 1 \text{ mol } (-553.5 \text{ kJ} \cdot \text{mol}^{-1})]$$

$$- [1 \text{ mol } (-1128.8 \text{ kJ} \cdot \text{mol}^{-1}) + 2 \text{ mol } (0 \text{ kJ} \cdot \text{mol}^{-1})]$$

$$\Delta G^\circ = -56.2 \text{ kJ}$$

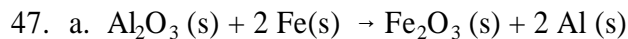
45. a. spontaneous as written

b. spontaneous as written

c. non-spontaneous as written

d. $K = 0.048$, significant concentrations of reactants and products

e. non-spontaneous as written



$$\Delta H^\circ = [1 \text{ mol } (\Delta H_f^\circ (\text{Fe}_2\text{O}_3(\text{s}))) + 2 \text{ mol } (\Delta H_f^\circ (\text{Al}(\text{s})))]$$

$$- [1 \text{ mol } (\Delta H_f^\circ (\text{Al}_2\text{O}_3(\text{s}))) + 2 \text{ mol } (\Delta H_f^\circ (\text{Fe}(\text{s})))]$$

$$\Delta H^\circ = [1 \text{ mol } (-825.5 \text{ kJ} \cdot \text{mol}^{-1}) + 2 \text{ mol } (0 \text{ kJ} \cdot \text{mol}^{-1})]$$

$$- [1 \text{ mol } (-1675.7 \text{ kJ} \cdot \text{mol}^{-1}) + 2 \text{ mol } (0 \text{ kJ} \cdot \text{mol}^{-1})] = 850.2 \text{ kJ}$$

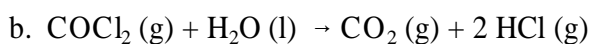
$$\Delta G^\circ = [1 \text{ mol } (\Delta G_f^\circ (\text{Fe}_2\text{O}_3 (\text{s}))) + 2 \text{ mol } (\Delta G_f^\circ (\text{Al} (\text{s})))]$$

$$- [1 \text{ mol } (\Delta G_f^\circ (\text{Al}_2\text{O}_3 (\text{s}))) + 2 \text{ mol } (\Delta G_f^\circ (\text{Fe} (\text{s})))]$$

$$\Delta G^\circ = [1 \text{ mol } (-743.5 \text{ kJ} \cdot \text{mol}^{-1}) + 2 \text{ mol } (0 \text{ kJ} \cdot \text{mol}^{-1})]$$

$$- [1 \text{ mol } (-1582.3 \text{ kJ} \cdot \text{mol}^{-1}) + 2 \text{ mol } (0 \text{ kJ} \cdot \text{mol}^{-1})] = 838.8 \text{ kJ}$$

The reaction is endothermic and absorbs 850. kJ of heat for every mole of Fe_2O_3 produced. The large positive value of ΔG° indicates that it is a very unfavorable reaction as written.



$$\Delta H^\circ = [1 \text{ mol } (\Delta H_f^\circ (\text{CO}_2 (\text{g}))) + 2 \text{ mol } (\Delta H_f^\circ (\text{HCl} (\text{g})))]$$

$$- [1 \text{ mol } (\Delta H_f^\circ (\text{COCl}_2 (\text{g}))) + 1 \text{ mol } (\Delta H_f^\circ (\text{H}_2\text{O} (\text{l})))]$$

$$\Delta H^\circ = [1 \text{ mol } (-393.5 \text{ kJ} \cdot \text{mol}^{-1}) + 2 \text{ mol } (-92.31 \text{ kJ} \cdot \text{mol}^{-1})]$$

$$- [1 \text{ mol } (-220.1 \text{ kJ} \cdot \text{mol}^{-1}) + 1 \text{ mol } (-285.8 \text{ kJ} \cdot \text{mol}^{-1})] = -72.2 \text{ kJ}$$

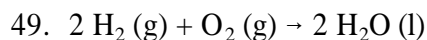
$$\Delta G^\circ = [1 \text{ mol } (\Delta G_f^\circ (\text{CO}_2 (\text{g}))) + 2 \text{ mol } (\Delta G_f^\circ (\text{HCl} (\text{g})))]$$

$$- [1 \text{ mol } (\Delta G_f^\circ (\text{COCl}_2 (\text{g}))) + 1 \text{ mol } (\Delta G_f^\circ (\text{H}_2\text{O} (\text{l})))]$$

$$\Delta G^\circ = [1 \text{ mol } (-394.4 \text{ kJ} \cdot \text{mol}^{-1}) + 2 \text{ mol } (-95.30 \text{ kJ} \cdot \text{mol}^{-1})]$$

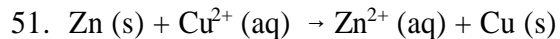
$$- [1 \text{ mol } (-205.9 \text{ kJ} \cdot \text{mol}^{-1}) + 1 \text{ mol } (-237.1 \text{ kJ} \cdot \text{mol}^{-1})] = -142.0 \text{ kJ}$$

The reaction is exothermic, liberating 72 kJ of heat and the negative sign of ΔG° indicates that the reaction is favorable.



$$\Delta G^\circ = 2 \text{ mol } (\Delta G_f^\circ (\text{H}_2\text{O} (\text{l}))) = 2 \text{ mol } (-237.1 \text{ kJ} \cdot \text{mol}^{-1}) = -474.2 \text{ kJ}$$

If the maximum amount of useful work is obtained, it will be $\Delta G^\circ = -474.2 \text{ kJ}$. Under these conditions, no entropy is produced.



$$4.85 \text{ g Zn} \times \frac{1 \text{ mol Zn}}{65.39 \text{ g}} = 0.07417 \text{ mol Zn}$$

$$\Delta G^\circ = 0.07417 \text{ mol } (\Delta G_f^\circ (\text{Zn}^{2+} \text{ (aq)})) - 0.07417 \text{ mol } (\Delta G_f^\circ (\text{Cu}^{2+} \text{ (aq)}))$$

$$\Delta G^\circ = 0.07417 \text{ mol } (-147.0 \text{ kJ} \cdot \text{mol}^{-1}) - 0.07417 \text{ mol } (+65.52 \text{ kJ} \cdot \text{mol}^{-1}) = -15.8 \text{ kJ}$$

The maximum useful work is -15.8 kJ and no entropy is produced.

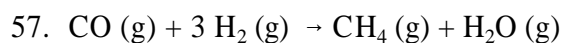
53. a. $K = \frac{P_{\text{CO}_2} P_{\text{H}_2}}{P_{\text{CO}} P_{\text{H}_2\text{O}}}$

b. $K = [\text{Mg}^{2+}][\text{OH}^-]^2$

c. $K = [\text{Li}^+]^2[\text{OH}^-]^2 P_{\text{H}_2}$

55. $\Delta G^\circ = 2 \text{ mol } (\Delta G_f^\circ (\text{HBr (g)})) = 2 \text{ mol } (-53.50 \text{ kJ} \cdot \text{mol}^{-1}) = -107.0 \text{ kJ}$

$$K = e^{\frac{-\Delta G^\circ}{RT}} = e^{\frac{-(-107,000 \text{ J})}{(8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}})(298 \text{ K})}} = 5.7 \times 10^{18}$$



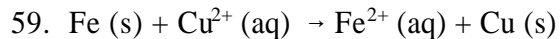
$$\Delta G^\circ = [1 \text{ mol } (\Delta G_f^\circ (\text{CH}_4 \text{ (g)})) + 1 \text{ mol } (\Delta G_f^\circ (\text{H}_2\text{O (g)}))]$$

$$- [1 \text{ mol } (\Delta G_f^\circ (\text{CO (g)})) + 3 \text{ mol } (\Delta G_f^\circ (\text{H}_2 \text{ (g)}))]$$

$$\Delta G^\circ = [1 \text{ mol } (-50.80 \text{ kJ} \cdot \text{mol}^{-1}) + 1 \text{ mol } (-228.6 \text{ kJ} \cdot \text{mol}^{-1})]$$

$$- [1 \text{ mol } (-137.2 \text{ kJ} \cdot \text{mol}^{-1}) + 3 \text{ mol } (0 \text{ kJ} \cdot \text{mol}^{-1})] = -142.2 \text{ kJ}$$

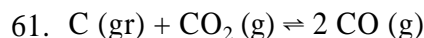
$$K = e^{\frac{-\Delta G^\circ}{RT}} = e^{\frac{-(-142,200 \text{ J})}{(8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}})(298 \text{ K})}} = 8.4 \times 10^{24}$$



$$\Delta G^\circ = 1 \text{ mol } (\Delta G_f^\circ (\text{Fe}^{2+} (\text{aq}))) - 1 \text{ mol } (\Delta G_f^\circ (\text{Cu}^{2+} (\text{aq})))$$

$$\Delta G^\circ = 1 \text{ mol } (-78.87 \text{ kJ} \cdot \text{mol}^{-1}) - 1 \text{ mol } (+65.52 \text{ kJ} \cdot \text{mol}^{-1}) = -144.39 \text{ kJ} = -144,390 \text{ J}$$

$$K = e^{\frac{-\Delta G^\circ}{RT}} = e^{\frac{-(-144,390 \text{ J})}{(8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}})(298 \text{ K})}} = 2.0 \times 10^{26}$$



$$\Delta H^\circ = [2 \text{ mol } (\Delta H_f^\circ (\text{CO (g)}))] - [1 \text{ mol } (\Delta H_f^\circ (\text{CO}_2 (\text{g}))) + 1 \text{ mol } (\Delta H_f^\circ (\text{C (gr)}))]$$

$$\Delta H^\circ = [2 \text{ mol } (-110.5 \text{ kJ} \cdot \text{mol}^{-1})] - [1 \text{ mol } (-393.5 \text{ kJ} \cdot \text{mol}^{-1}) + 1 \text{ mol } (0 \text{ kJ} \cdot \text{mol}^{-1})] = +172.5 \text{ kJ}$$

$$\Delta S^\circ = [2 \text{ mol } (S^\circ (\text{CO (g)}))] - [1 \text{ mol } (S^\circ (\text{CO}_2 (\text{g}))) + 1 \text{ mol } (S^\circ (\text{C (gr)}))]$$

$$\Delta S^\circ = [2 \text{ mol } (+197.5 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})]$$

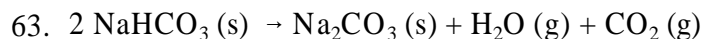
$$- [1 \text{ mol } (+213.7 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}) + 1 \text{ mol } (+5.740 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})]$$

$$\Delta S^\circ = +175.56 \text{ J} \cdot \text{K}^{-1} = 0.17556 \text{ kJ} \cdot \text{K}^{-1}$$

$$\Delta G^\circ_T = \Delta H^\circ - T\Delta S^\circ = +172.5 \text{ kJ} - 1273 \text{ K } (+0.1756 \text{ kJ} \cdot \text{K}^{-1}) = 50.98 \text{ kJ} = 5.098 \times 10^3 \text{ J}$$

$$K = e^{\frac{-\Delta G^\circ}{RT}} = e^{\frac{-(-50,980 \text{ J})}{(8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}})(1273 \text{ K})}} = 1.2 \times 10^2$$

Since the values of ΔH and ΔS are both positive, the equilibrium should become more favorable at higher temperatures. At 1273 K (1000°C) K_p is 120, indicating a significant partial pressure of CO.



$$\Delta H^\circ = [1 \text{ mol } (\Delta H_f^\circ (\text{Na}_2\text{CO}_3 (\text{s}))) + 1 \text{ mol } (\Delta H_f^\circ (\text{H}_2\text{O (g)})) + 1 \text{ mol } (\Delta H_f^\circ (\text{CO}_2 (\text{g})))]$$

$$- 2 \text{ mol } (\Delta H_f^\circ (\text{NaHCO}_3 (\text{s})))$$

$$\Delta H^\circ = [1 \text{ mol } (-1130.8 \text{ kJ} \cdot \text{mol}^{-1})] + [1 \text{ mol } (-241.8 \text{ kJ} \cdot \text{mol}^{-1}) + 1 \text{ mol } (-393.5 \text{ kJ} \cdot \text{mol}^{-1})]$$

$$- 2 \text{ mol } (-950.8 \text{ kJ} \cdot \text{mol}^{-1}) = +135.5 \text{ kJ} = 135,500 \text{ J}$$

$$\Delta S^\circ = [1 \text{ mol } (S^\circ (\text{Na}_2\text{CO}_3 (\text{s}))) + 1 \text{ mol } (S^\circ (\text{H}_2\text{O} (\text{g}))) + 1 \text{ mol } (S^\circ (\text{CO}_2 (\text{g})))]$$

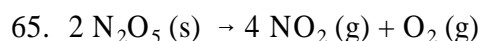
$$- 2 \text{ mol } (S^\circ (\text{NaHCO}_3 (\text{s})))$$

$$\Delta S^\circ = [1 \text{ mol } (+138.8 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}) + 1 \text{ mol } (+188.7 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})$$

$$+ 1 \text{ mol } (+213.7 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})] - 2 \text{ mol } (+101.7 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}) = +337.8 \text{ J} \cdot \text{K}^{-1}$$

$$\Delta G^\circ = 0 = \Delta H^\circ - T\Delta S^\circ$$

$$T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{135,500 \text{ J}}{337.8 \text{ J} \cdot \text{K}^{-1}} = 401.1 \text{ K} = 128.0^\circ\text{C}$$



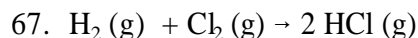
Since 5 moles of gas are formed at the expense of two moles of a solid, the sign of ΔS should be large and positive. ($S^\circ \text{ N}_2\text{O}_5 (\text{s}) = +178.2 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$) We can calculate the actual value of ΔS° from this value and the data in Appendix C.

$$\Delta S^\circ = [4 \text{ mol } (S^\circ (\text{NO}_2 (\text{g}))) + 1 \text{ mol } (S^\circ (\text{O}_2 (\text{g}))) - 2 \text{ mol } (S^\circ \text{ N}_2\text{O}_5 (\text{s}))]$$

$$\Delta S^\circ = [4 \text{ mol } (+239.9 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}) + 1 \text{ mol } (+205.0 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})$$

$$- 2 \text{ mol } (+178.2 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})] = +808.2 \text{ J} \cdot \text{K}^{-1}$$

The fact that the reaction is spontaneous despite being endothermic implies that the $T\Delta S$ term is larger in than ΔH , making ΔG negative.



$$\Delta H \approx \text{B.E. (H-H)} + \text{B.E. (Cl-Cl)} - 2 \text{ B.E. H-Cl}$$

$$\Delta H \approx 1 \text{ mol } (432 \text{ kJ} \cdot \text{mol}^{-1}) + 1 \text{ mol } (240 \text{ kJ} \cdot \text{mol}^{-1}) - 2 \text{ mol } (428 \text{ kJ} \cdot \text{mol}^{-1}) = -184 \text{ kJ}$$

The reaction should be exothermic. The sign of ΔS should be positive, because there are more ways to assemble the products than to assemble the reactants. ΔS° is, in fact, $\sim 20 \text{ J} \cdot \text{K}^{-1}$. A negative ΔH and a positive ΔS lead to a spontaneous reaction at all temperatures.

69. When acetic acid freezes, $\Delta H = -\Delta H_{\text{fus}}$.

$$\Delta H^\circ = -69.0 \frac{\text{J}}{\text{g}} \times 60.05 \frac{\text{g}}{\text{mol}} = -4.14 \times 10^3 \frac{\text{J}}{\text{mol}}$$

$$\Delta S^\circ = \frac{\Delta H^\circ}{T} = \frac{-4140 \text{ J}}{289.8 \text{ K}} = -14.3 \frac{\text{J}}{\text{K} \cdot \text{mol}}$$

71. a. ΔS should be negative
 b. ΔS should be positive
 c. ΔS should be positive
 d. ΔS should be negative

73. ΔS should be negative since there is a net decrease in the number of moles of gas.

75. $\text{C}_2\text{H}_5\text{OH} (\text{l}) + \text{O}_2 (\text{g}) \rightarrow \text{CH}_3\text{COOH} (\text{l}) + \text{H}_2\text{O} (\text{l})$

$$\Delta S^\circ = [1 \text{ mol } (S^\circ (\text{CH}_3\text{COOH} (\text{l}))) + 1 \text{ mol } (S^\circ (\text{H}_2\text{O} (\text{l})))]$$

$$- [1 \text{ mol } (S^\circ (\text{C}_2\text{H}_5\text{OH} (\text{l}))) + 1 \text{ mol } (S^\circ (\text{O}_2 (\text{g})))]$$

$$\Delta S^\circ = [1 \text{ mol } (+159.8 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}) + 1 \text{ mol } (+69.95 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})]$$

$$- [1 \text{ mol } (+160.7 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}) + 1 \text{ mol } (+205.0 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})]$$

$$\Delta S^\circ = -136.0 \text{ J} \cdot \text{K}^{-1}$$

77. $\text{SO}_2 (\text{g}) + \text{H}_2 (\text{g}) \rightarrow \text{H}_2\text{S} (\text{g}) + \text{O}_2 (\text{g})$

$$\Delta G^\circ = [1 \text{ mol } (\Delta G_f^\circ (\text{H}_2\text{S} (\text{g}))) + 1 \text{ mol } (\Delta G_f^\circ (\text{O}_2 (\text{g})))]$$

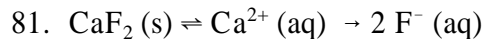
$$- [1 \text{ mol } (\Delta G_f^\circ (\text{SO}_2 (\text{g}))) + 1 \text{ mol } (\Delta G_f^\circ (\text{H}_2 (\text{g})))]$$

$$\Delta G^\circ = [1 \text{ mol } (-33.33 \text{ kJ} \cdot \text{mol}^{-1}) + 1 \text{ mol } (0 \text{ kJ} \cdot \text{mol}^{-1})]$$

$$- [1 \text{ mol } (-300.1 \text{ kJ} \cdot \text{mol}^{-1}) + 1 \text{ mol } (0 \text{ kJ} \cdot \text{mol}^{-1})] = +266.8 \text{ kJ}$$

The reaction, as written, is non-spontaneous at 25°C because ΔG° is positive.

79. At lower temperatures, the ΔH term is more important, but at higher temperatures, the $T\Delta S$ term begins to outweigh the ΔH term. The fact that the reaction is non-spontaneous at lower temperatures and becomes spontaneous at higher temperatures implies that both ΔH and ΔS are positive.

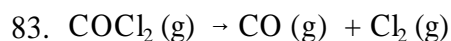


$$\Delta G^{\circ} = [1 \text{ mol } (\Delta G_{\text{f}}^{\circ}(\text{Ca}^{2+}(\text{aq}))) + 2 \text{ mol } (\Delta G_{\text{f}}^{\circ}(\text{F}^{-}(\text{aq})))] - 1 \text{ mol } (\Delta G_{\text{f}}^{\circ}(\text{CaF}_2(\text{s})))$$

$$\Delta G^{\circ} = [1 \text{ mol } (-553.5 \text{ kJ} \cdot \text{mol}^{-1}) + 2 \text{ mol } (-278.8 \text{ kJ} \cdot \text{mol}^{-1})] - 1 \text{ mol } (-1173.5 \text{ kJ} \cdot \text{mol}^{-1})$$

$$\Delta G^{\circ} = 62.4 \text{ kJ}$$

$$K = e^{\frac{-\Delta G^{\circ}}{RT}} = e^{\frac{-62,400 \text{ J}}{(8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}})(298 \text{ K})}} = 1 \times 10^{-11}$$



$$\Delta H^{\circ} = [1 \text{ mol } (\Delta H_{\text{f}}^{\circ}(\text{CO}(\text{g}))) + 1 \text{ mol } (\Delta H_{\text{f}}^{\circ}(\text{Cl}_2(\text{g})))] - 1 \text{ mol } (\Delta H_{\text{f}}^{\circ}(\text{COCl}_2(\text{g})))$$

$$\Delta H^{\circ} = [1 \text{ mol } (-110.5 \text{ kJ} \cdot \text{mol}^{-1}) + 1 \text{ mol } (0 \text{ kJ} \cdot \text{mol}^{-1})] - 1 \text{ mol } (-220.1 \text{ kJ} \cdot \text{mol}^{-1})$$

$$\Delta H^{\circ} = 109.6 \text{ kJ}$$

$$\Delta S^{\circ} = [1 \text{ mol } (S^{\circ}(\text{CO}(\text{g}))) + 1 \text{ mol } (S^{\circ}(\text{Cl}_2(\text{g})))] - 1 \text{ mol } (S^{\circ}(\text{COCl}_2(\text{g})))$$

$$\Delta S^{\circ} = [1 \text{ mol } (+197.5 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}) + 1 \text{ mol } (+223.0 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})]$$

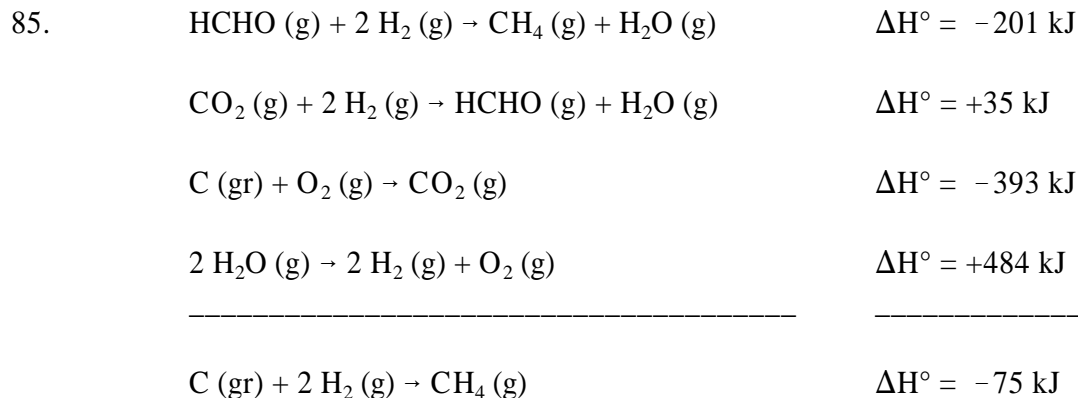
$$- 1 \text{ mol } (+283.9 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})$$

$$\Delta S^{\circ} = +136.6 \text{ J} \cdot \text{K}^{-1} = +0.1366 \text{ kJ} \cdot \text{K}^{-1}$$

At 25°C: $\Delta G^{\circ} = 109.6 \text{ kJ} - 298 \text{ K } (0.1366 \text{ kJ} \cdot \text{K}^{-1}) = +68.9 \text{ kJ}$

At 800°C: $\Delta G^{\circ} = 109.6 \text{ kJ} - 1073 \text{ K } (0.1366 \text{ kJ} \cdot \text{K}^{-1}) = -37.0 \text{ kJ}$

The reaction is non-spontaneous at room temperature, but becomes spontaneous at higher temperature. This is characteristic of reactions that have positive values of ΔH° and ΔS° .



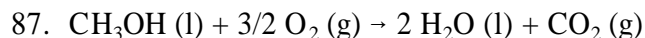
$$\Delta S^\circ = [1 \text{ mol } (S^\circ (\text{CH}_4 \text{(g)}))] - [2 \text{ mol } (S^\circ (\text{H}_2 \text{(g)})) + 1 \text{ mol } (S^\circ (\text{C}(\text{gr})))]$$

$$\Delta S^\circ = [1 \text{ mol } (+186.1 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})]$$

$$- [2 \text{ mol } (+130.6 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}) + 1 \text{ mol } (+5.740 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})]$$

$$\Delta S^\circ = -80.8 \text{ J} \cdot \text{K}^{-1} = -0.0808 \text{ kJ} \cdot \text{K}^{-1}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -75 \text{ kJ} - 298 \text{ K } (-0.0808 \text{ kJ} \cdot \text{K}^{-1}) = -51 \text{ kJ} = \Delta G_f^\circ (\text{CH}_4 \text{(g)})$$



$$\Delta H^\circ = 1 \text{ mol } (-393.5 \text{ kJ} \cdot \text{mol}^{-1}) + 2 \text{ mol } (-285.8 \text{ kJ} \cdot \text{mol}^{-1}) - 1 \text{ mol } (-238.7 \text{ kJ} \cdot \text{mol}^{-1})$$

$$\Delta H^\circ = -726.4 \text{ kJ}$$

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T} = \frac{-726,400 \text{ J} - (-702,200 \text{ J})}{298 \text{ K}} = -81.2 \text{ J} \cdot \text{K}^{-1}$$

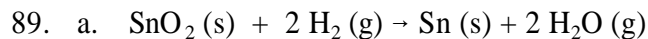
$$\Delta S^\circ = -80.2 \text{ J} \cdot \text{K}^{-1} = [1 \text{ mol } (S^\circ (\text{CO}_2 \text{(g)})) + 2 \text{ mol } (S^\circ (\text{H}_2\text{O (l)}))]$$

$$- [1 \text{ mol } (S^\circ (\text{CH}_3\text{OH (l)})) + 3/2 \text{ mol } (S^\circ (\text{O}_2 \text{(g)}))]$$

$$-81.2 \text{ J} \cdot \text{K}^{-1} = [1 \text{ mol } (+213.7 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}) + 2 \text{ mol } (+70.0 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})]$$

$$- [1 \text{ mol } (+126.8 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}) + 3/2 \text{ mol } (S^\circ (\text{O}_2 \text{(g)}))]$$

$$S^\circ (\text{O}_2 \text{(g)}) = \mathbf{b} (+81.2 \text{ J} \cdot \text{K}^{-1} + 213.7 \text{ J} \cdot \text{K}^{-1} + 140.0 \text{ J} \cdot \text{K}^{-1} - 126.8 \text{ J} \cdot \text{K}^{-1}) = 205.4 \text{ J} \cdot \text{K}^{-1}$$



$$\Delta H^\circ = [2 \text{ mol } (\Delta H_f^\circ (\text{H}_2\text{O}(\text{g}))) + 1 \text{ mol } (\Delta H_f^\circ (\text{Sn}(\text{s}, \text{white})))]$$

$$- [2 \text{ mol } (\Delta H_f^\circ (\text{H}_2(\text{g}))) + 1 \text{ mol } (\Delta H_f^\circ (\text{SnO}_2(\text{s})))]$$

$$\Delta H^\circ = [2 \text{ mol } (-241.8 \text{ kJ} \cdot \text{mol}^{-1}) + 1 \text{ mol } (0 \text{ kJ} \cdot \text{mol}^{-1})]$$

$$- [2 \text{ mol } (0 \text{ kJ} \cdot \text{mol}^{-1}) + 1 \text{ mol } (-580.7 \text{ kJ} \cdot \text{mol}^{-1})]$$

$$\Delta H^\circ = +97.1 \text{ kJ}$$

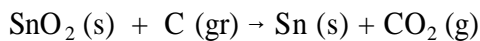
$$\Delta S^\circ = [2 \text{ mol } (S^\circ (\text{H}_2\text{O}(\text{g}))) + 1 \text{ mol } (S^\circ (\text{Sn}(\text{s})))]$$

$$- [2 \text{ mol } (S^\circ (\text{H}_2(\text{g}))) + 1 \text{ mol } (S^\circ (\text{SnO}_2(\text{white}, \text{s})))]$$

$$\Delta S^\circ = [2 \text{ mol } (+188.7 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}) + 1 \text{ mol } (+51.55 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})]$$

$$- [2 \text{ mol } (+130.6 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}) + 1 \text{ mol } (+52.3 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})]$$

$$\Delta S^\circ = +115.4 \text{ J} \cdot \text{K}^{-1}$$



$$\Delta H^\circ = [1 \text{ mol } (\Delta H_f^\circ (\text{CO}_2(\text{g}))) + 1 \text{ mol } (\Delta H_f^\circ (\text{Sn}(\text{white}, \text{s})))]$$

$$- [1 \text{ mol } (\Delta H_f^\circ (\text{C}(\text{gr}))) + 1 \text{ mol } (\Delta H_f^\circ (\text{SnO}_2(\text{s})))]$$

$$\Delta H^\circ = [1 \text{ mol } (-393.5 \text{ kJ} \cdot \text{mol}^{-1}) + 1 \text{ mol } (0 \text{ kJ} \cdot \text{mol}^{-1})]$$

$$- [1 \text{ mol } (0 \text{ kJ} \cdot \text{mol}^{-1}) + 1 \text{ mol } (-580.7 \text{ kJ} \cdot \text{mol}^{-1})]$$

$$\Delta H^\circ = +187.2 \text{ kJ}$$

$$\Delta S^\circ = [1 \text{ mol } (S^\circ (\text{CO}_2(\text{g}))) + 1 \text{ mol } (S^\circ (\text{Sn}(\text{s}, \text{white})))]$$

$$- [1 \text{ mol } (S^\circ (\text{C}(\text{gr}))) + 1 \text{ mol } (S^\circ (\text{SnO}_2(\text{g})))]$$

$$\Delta S^\circ = [1 \text{ mol } (+213.7 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}) + 1 \text{ mol } (+51.55 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})]$$

$$- [1 \text{ mol } (+5.740 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}) + 1 \text{ mol } (+52.3 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})]$$

$$\Delta S^\circ = +207.2 \text{ J} \cdot \text{K}^{-1}$$

b. For the process with H₂, the temperature above which the reaction is spontaneous is:

$$T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{97,100 \text{ J}}{115.4 \text{ J} \cdot \text{K}^{-1}} = 841 \text{ K} = 567^\circ\text{C}$$

For the process with graphite, the temperature above which the reaction is spontaneous is:

$$T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{187,200 \text{ J}}{207.2 \text{ J} \cdot \text{K}^{-1}} = 903 \text{ K} = 630.^\circ\text{C}$$

c. On the basis of temperature alone, the hydrogen reduction would be preferred. However, H₂ is much more expensive to use as a reducing agent than graphite, so industrially the process is carried out using graphite as the reducing agent.

91. a. The fact that the reaction is endothermic implies the products are at higher energy than the reactants. Energetically, the reactants are favored.

b. Because a mole of gas and a mole of liquid are formed from a mole of liquid, ΔS should be positive. Entropically, the products are favored.

93. a. Since ΔG is negative, the products are favored at equilibrium.

b. The reaction system must be heated so that the reaction occurs at a reasonable rate. There is an activation barrier to the reaction which is overcome by heating the reaction mixture.

95. $\text{C}_4\text{H}_{10}(\text{g}) + 13/2 \text{O}_2(\text{g}) \rightarrow 4 \text{CO}_2(\text{g}) + 5 \text{H}_2\text{O}(\text{l})$

$$\Delta H = \frac{-49.50 \text{ kJ}}{1.000 \text{ g}} \times \frac{58.12 \text{ g}}{1 \text{ mol}} = -2877 \frac{\text{kJ}}{\text{mol}}$$

a. $-2877 \text{ kJ} = 4 \text{ mol} (-393.5 \text{ kJ} \cdot \text{mol}^{-1}) + 5 \text{ mol} (-285.8 \text{ kJ} \cdot \text{mol}^{-1}) - 1 \text{ mol} (\Delta H_f^\circ (\text{C}_4\text{H}_{10}(\text{g})))$

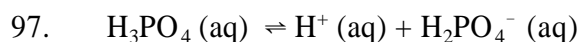
$$\Delta H_f^\circ (\text{C}_4\text{H}_{10}(\text{g})) = -126 \text{ kJ mol}^{-1}$$

b. $\Delta G^\circ = 4 \text{ mol} (-394.4 \text{ kJ} \cdot \text{mol}^{-1}) + 5 \text{ mol} (-237.1 \text{ kJ} \cdot \text{mol}^{-1}) - 1 \text{ mol} (-17.2 \text{ kJ} \cdot \text{mol}^{-1})$

$$\Delta G^\circ = -2745.9 \text{ kJ}$$

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

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T} = \frac{-2,877,000 \text{ J} - (-2,745,900 \text{ J})}{298 \text{ K}} = -440. \text{ J} \cdot \text{K}^{-1}$$



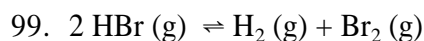
$$\Delta H^\circ = 1 \text{ mol} (-1285 \text{ kJ} \cdot \text{mol}^{-1}) - 1 \text{ mol} (-1288.3 \text{ kJ} \cdot \text{mol}^{-1}) = +3.3 \text{ kJ}$$

$$\Delta S^\circ = 1 \text{ mol} (89 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}) - 1 \text{ mol} (158.2 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}) = -69.2 \text{ J} \cdot \text{K}^{-1}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = +3,300 \text{ J} - 298 \text{ K} (-69.2 \text{ J} \cdot \text{K}^{-1}) = +23,900 \text{ J} = +23.9 \text{ J}$$

$$K = e^{\frac{-\Delta G^\circ}{RT}} = e^{\frac{-23,900 \text{ J}}{(8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}})(298 \text{ K})}} = 6.4 \times 10^{-5}$$

The unfavorable entropic term and, to a lesser extent, the unfavorable enthalpic term are responsible for the positive value of ΔG° , $K < 1$, and therefore the fact that phosphoric acid is a weak acid. The negative value of ΔS° implies that the products are more ordered than the reactants. This is because the ions in solution tend to order the water molecules due to ion-dipole interactions.



$$\Delta H^\circ = [1 \text{ mol} (\Delta H_f^\circ (\text{H}_2(\text{g}))) + 1 \text{ mol} (\Delta H_f^\circ (\text{Br}_2(\text{g})))] - 2 \text{ mol} (\Delta H_f^\circ (\text{HBr}(\text{g})))$$

$$\Delta H^\circ = [1 \text{ mol} (0 \text{ kJ} \cdot \text{mol}^{-1}) + 1 \text{ mol} (+30.91 \text{ kJ} \cdot \text{mol}^{-1})] - 2 \text{ mol} (-36.44 \text{ kJ} \cdot \text{mol}^{-1})$$

$$\Delta H^\circ = +103.79 \text{ kJ}$$

$$\Delta S^\circ = [1 \text{ mol} (S^\circ (\text{H}_2(\text{g}))) + 1 \text{ mol} (S^\circ (\text{Br}_2(\text{g})))] - 2 \text{ mol} (S^\circ (\text{HBr}(\text{g})))$$

$$\Delta S^\circ = [1 \text{ mol} (+130.6 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}) + 1 \text{ mol} (+245.3 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})] - 2 \text{ mol} (+198.6 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})$$

$$\Delta S^\circ = -21.3 \text{ J} \cdot \text{K}^{-1}$$

At 375°C:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = +103,790 \text{ J} - 648 \text{ K} (-21.3 \text{ J} \cdot \text{K}^{-1}) = +117,600 \text{ J}$$

$$K = e^{\frac{-\Delta G^\circ}{RT}} = e^{\frac{-117,600 \text{ J}}{(8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}})(648 \text{ K})}} = 3.3 \times 10^{-10}$$

	2 HBr (g)	\rightleftharpoons	H ₂ (g) +	Br ₂ (g)
P _i	1.00		0	0
ΔP	-2x		+x	+x
P _{eq}	1.00 - 2x		x	x

$$K_p = \frac{P_{\text{H}_2} P_{\text{Br}_2}}{P_{\text{HBr}}^2} = \frac{x^2}{(1.00 - 2x)^2} = 3.3 \times 10^{-10}$$

Assume $2x \ll 1.0$

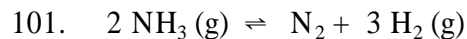
$$\frac{x^2}{(1.00)^2} = 3.3 \times 10^{-10}$$

$$x = \sqrt{3.3 \times 10^{-10}} = 1.8 \times 10^{-5} \text{ atm}$$

$$\frac{2(1.8 \times 10^{-5})}{1.00} \times 100 = 0.004\% \quad (\text{assumption is justified})$$

$$\% \text{ dissociation} = \frac{2(1.8 \times 10^{-5})}{1.00} \times 100 = 0.004\%$$

On the basis of LeChatelier's Principle, we can say that the total pressure will not affect the equilibrium because there are 2 moles of gas on both sides of the equilibrium.



$$\Delta H^\circ = [1 \text{ mol } (\Delta H_f^\circ (\text{N}_2(\text{g}))) + 3 \text{ mol } (\Delta H_f^\circ (\text{H}_2(\text{g})))] - 2 \text{ mol } (\Delta H_f^\circ (\text{NH}_3(\text{g})))$$

$$\Delta H^\circ = [1 \text{ mol } (0 \text{ kJ} \cdot \text{mol}^{-1}) + 3 \text{ mol } (0 \text{ kJ} \cdot \text{mol}^{-1})] - 2 \text{ mol } (-45.90 \text{ kJ} \cdot \text{mol}^{-1})$$

$$\Delta H^\circ = +91.80 \text{ kJ}$$

$$\Delta S^\circ = [1 \text{ mol } (S^\circ (\text{N}_2(\text{g}))) + 3 \text{ mol } (S^\circ (\text{H}_2(\text{g})))] - 2 \text{ mol } (S^\circ (\text{NH}_3(\text{g})))$$

$$\Delta S^\circ = [1 \text{ mol } (+191.6 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}) + 3 \text{ mol } (+130.6 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})] - 2 \text{ mol } (+192.7 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})$$

$$\Delta S^\circ = +198.0 \text{ J} \cdot \text{K}^{-1}$$

At 345°C:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = +91.80 \text{ kJ} - 618 \text{ K } (+0.1980 \text{ kJ} \cdot \text{K}^{-1}) = -30560 \text{ J}$$

$$K_p = e^{\frac{-\Delta G^\circ}{RT}} = e^{\frac{-(-30560 \text{ J})}{(8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}})(618 \text{ K})}} = 3.8 \times 10^2$$

$$K_c = K_p (RT)^{-\Delta n} = 3.8 \times 10^2 \times (0.082056 \times 618)^{-2} = 0.14$$

	2 NH ₃ (g)	\rightleftharpoons	N ₂ (g) +	3 H ₂ (g)
[] _i	0.0500		0	0
Δ []	-2x		+x	+3x
[] _{eq}	0.0500 - 2x		x	3x

$$K_c = \frac{[\text{N}_2][\text{H}_2]^3}{[\text{NH}_3]^2} = \frac{(x)(3x)^3}{(0.0500 - 2x)^2} = 0.14 = \frac{27x^4}{(0.0500 - 2x)^2}$$

$$\sqrt{\frac{0.14}{27}} = \frac{x^2}{(0.0500 - 2x)} = 0.072 \quad x^2 + 0.144x - 0.0036 = 0$$

The roots are 0.021 and -0.16, the second of which is rejected.

$$[\text{NH}_3] = 0.0500 - 2(0.021) = 0.008 \text{ M}$$

$$[\text{N}_2] = 0.021 \text{ M}$$

$$[\text{H}_2] = 0.063 \text{ M}$$

$$\% \text{ dissociation} = \frac{2(0.021)}{0.0500} \times 100 = \underline{84} \%$$