

AP Chemistry – Principles of Reactivity: Entropy and Free Energy (Kotz – 19)
Homework Answers 3, 5, 8, 9, 13, 17, 19, 22, 26, 27, 32, 33, 44, 50

- 19.3 (a) $\text{CH}_3\text{OH}(\text{g})$ has a higher entropy than $\text{O}_2(\text{g})$
(b) $\text{HBr}(\text{g})$ has a higher entropy than $\text{HCl}(\text{g})$ or $\text{HF}(\text{g})$
(c) $\text{NH}_4\text{Cl}(\text{aq})$ has a higher entropy than $\text{NH}_4\text{Cl}(\text{s})$
(d) $\text{HNO}_3(\text{g})$ has a higher entropy than $\text{HNO}_3(\ell)$ or $\text{HNO}_3(\text{aq})$

- 19.5 (a) $\Delta S^\circ = S^\circ[\text{KOH}(\text{aq})] - S^\circ[\text{KOH}(\text{s})]$
 $\Delta S^\circ = 1 \text{ mol } (91.6 \text{ J/K}\cdot\text{mol}) - 1 \text{ mol } (78.9 \text{ J/K}\cdot\text{mol}) = 12.7 \text{ J/K}$
A positive ΔS° indicates an increase in entropy
(b) $\Delta S^\circ = S^\circ[\text{Na}(\text{s})] - S^\circ[\text{Na}(\text{g})]$
 $\Delta S^\circ = 1 \text{ mol } (51.21 \text{ J/K}\cdot\text{mol}) - 1 \text{ mol } (153.765 \text{ J/K}\cdot\text{mol}) = -102.56 \text{ J/K}$
A negative ΔS° indicates a decrease in entropy
(c) $\Delta S^\circ = S^\circ[\text{Br}_2(\text{g})] - S^\circ[\text{Br}_2(\ell)]$
 $\Delta S^\circ = 1 \text{ mol } (245.42 \text{ J/K}\cdot\text{mol}) - 1 \text{ mol } (152.2 \text{ J/K}\cdot\text{mol}) = 93.2 \text{ J/K}$
A positive ΔS° indicates an increase in entropy
(d) $\Delta S^\circ = S^\circ[\text{HCl}(\text{aq})] - S^\circ[\text{HCl}(\text{g})]$
 $\Delta S^\circ = 1 \text{ mol } (56.5 \text{ J/K}\cdot\text{mol}) - 1 \text{ mol } (186.2 \text{ J/K}\cdot\text{mol}) = -129.7 \text{ J/K}$
A negative ΔS° indicates a decrease in entropy

- 19.8 $\Delta S^\circ = S^\circ[\text{NH}_3(\text{g})] - \{ \frac{1}{2} S^\circ[\text{N}_2(\text{g})] + \frac{3}{2} S^\circ[\text{H}_2(\text{g})] \}$
 $\Delta S^\circ = 1 \text{ mol } (192.77 \text{ J/K}\cdot\text{mol}) - [\frac{1}{2} \text{ mol } (191.56 \text{ J/K}\cdot\text{mol}) + \frac{3}{2} \text{ mol } (130.7 \text{ J/K}\cdot\text{mol})]$
 $\Delta S^\circ = -99.1 \text{ J/K}$

- 19.9 (a) $\frac{1}{2} \text{H}_2(\text{g}) + \frac{1}{2} \text{Cl}_2(\text{g}) \rightarrow \text{HCl}(\text{g})$
 $\Delta S^\circ = S^\circ[\text{HCl}(\text{g})] - \{ \frac{1}{2} S^\circ[\text{H}_2(\text{g})] + \frac{1}{2} S^\circ[\text{Cl}_2(\text{g})] \}$
 $\Delta S^\circ = 1 \text{ mol } (186.2 \text{ J/K}\cdot\text{mol}) - [\frac{1}{2} \text{ mol } (130.7 \text{ J/K}\cdot\text{mol}) + \frac{1}{2} \text{ mol } (223.08 \text{ J/K}\cdot\text{mol})]$
 $\Delta S^\circ = 9.3 \text{ J/K}$
(b) $\text{Ca}(\text{s}) + \text{O}_2(\text{g}) + \text{H}_2(\text{g}) \rightarrow \text{Ca}(\text{OH})_2(\text{s})$
 $\Delta S^\circ = S^\circ[\text{Ca}(\text{OH})_2(\text{s})] - \{ S^\circ[\text{Ca}(\text{s})] + S^\circ[\text{O}_2(\text{g})] + S^\circ[\text{H}_2(\text{g})] \}$
 $\Delta S^\circ = 1 \text{ mol } (83.39 \text{ J/K}\cdot\text{mol}) - [1 \text{ mol } (41.59 \text{ J/K}\cdot\text{mol}) + 1 \text{ mol } (205.07 \text{ J/K}\cdot\text{mol})$
 $\qquad\qquad\qquad + 1 \text{ mol } (130.7 \text{ J/K}\cdot\text{mol})]$
 $\Delta S^\circ = -294.0 \text{ J/K}$

- 19.13 $\Delta S^\circ_{\text{sys}} = S^\circ[\text{SiCl}_4(\text{g})] - \{ S^\circ[\text{Si}(\text{s})] + 2 S^\circ[\text{Cl}_2(\text{g})] \}$
 $\Delta S^\circ_{\text{sys}} = 1 \text{ mol } (330.86 \text{ J/K}\cdot\text{mol}) - [1 \text{ mol } (18.82 \text{ J/K}\cdot\text{mol}) + 2 \text{ mol } (223.08 \text{ J/K}\cdot\text{mol})]$
 $\Delta S^\circ_{\text{sys}} = -134.12 \text{ J/K}$
 $\Delta S^\circ_{\text{surr}} = -\Delta H^\circ_{\text{sys}}/T = -\Delta H_f^\circ[\text{SiCl}_4(\text{g})]/(298.15 \text{ K}) = -[1 \text{ mol } (-662.75 \text{ kJ/mol})/(298.15 \text{ K})] = 2.2229 \text{ kJ/K}$

$$\Delta S^{\circ}_{\text{univ}} = \Delta S^{\circ}_{\text{sys}} + \Delta S^{\circ}_{\text{surr}} = -134.12 \text{ J/K} + (2.2229 \text{ kJ/K})(10^3 \text{ J/1 kJ}) = 2088.8 \text{ J/K}$$

The reaction is spontaneous

19.17 (a) $\Delta H^{\circ} < 0$, $\Delta S^{\circ} < 0$; depends on T and relative magnitudes of ΔH and ΔS , more favorable at lower T .

(b) $\Delta H^{\circ} > 0$, $\Delta S^{\circ} < 0$; not spontaneous under all conditions

19.19 (a) $\Delta H^{\circ} = \Delta H_f^{\circ}[\text{MgO}(s)] + \Delta H_f^{\circ}[\text{CO}_2(g)] - \Delta H_f^{\circ}[\text{MgCO}_3(s)]$

$$\Delta H^{\circ} = 1 \text{ mol} (-601.24 \text{ kJ/mol}) + 1 \text{ mol} (-393.509 \text{ kJ/mol}) - 1 \text{ mol} (-1111.69 \text{ kJ/mol})$$

$$\Delta H^{\circ} = 116.94 \text{ kJ}$$

$$\Delta S^{\circ} = S^{\circ}[\text{MgO}(s)] + S^{\circ}[\text{CO}_2(g)] - S^{\circ}[\text{MgCO}_3(s)]$$

$$\Delta S^{\circ} = 1 \text{ mol} (26.85 \text{ J/K}\cdot\text{mol}) + 1 \text{ mol} (213.74 \text{ J/K}\cdot\text{mol}) - 1 \text{ mol} (65.84 \text{ J/K}\cdot\text{mol})$$

$$\Delta S^{\circ} = 174.75 \text{ J/K}$$

(b) $\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ} = 116.94 \text{ kJ} - (298 \text{ K})(174.75 \text{ J/K})(1 \text{ kJ}/10^3 \text{ J}) = 64.9 \text{ kJ}$

The reaction is predicted to be non-spontaneous at 298 K ($\Delta G^{\circ} > 0$)

(c) The reaction is predicted to be spontaneous at higher temperatures.

19.22 (a) $\Delta H^{\circ} = \Delta H_f^{\circ}[\text{Ca}(\text{OH})_2(\text{aq})] - 2 \Delta H_f^{\circ}[\text{H}_2\text{O}(\ell)]$

$$\Delta H^{\circ} = 1 \text{ mol} (-1002.82 \text{ kJ/mol}) - 2 \text{ mol} (-285.83 \text{ kJ/mol}) = -431.16 \text{ kJ}$$

$$\Delta S^{\circ} = S^{\circ}[\text{Ca}(\text{OH})_2(\text{aq})] + 2 S^{\circ}[\text{H}_2(\text{g})] - \{S^{\circ}[\text{Ca}(s)] + 2 S^{\circ}[\text{H}_2\text{O}(\ell)]\}$$

$$\Delta S^{\circ} = 1 \text{ mol} (-74.5 \text{ J/K}\cdot\text{mol}) + 2 \text{ mol} (130.7 \text{ J/K}\cdot\text{mol}) - [1 \text{ mol} (41.59 \text{ J/K}\cdot\text{mol})$$

$$+ 2 \text{ mol} (69.95 \text{ J/K}\cdot\text{mol})]$$

$$\Delta S^{\circ} = 5.41 \text{ J/K}$$

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ} = -431.16 \text{ kJ} - (298 \text{ K})(5.41 \text{ J/K})(1 \text{ kJ}/10^3 \text{ J}) = -432.8 \text{ kJ}$$

(b) $\Delta H^{\circ} = \Delta H_f^{\circ}[\text{C}_6\text{H}_6(\ell)] = 1 \text{ mol} (49.03 \text{ kJ/mol}) = 49.03 \text{ kJ}$

$$\Delta S^{\circ} = S^{\circ}[\text{C}_6\text{H}_6(\ell)] - \{6 S^{\circ}[\text{C}(\text{graphite})] + 3 S^{\circ}[\text{H}_2(\text{g})]\}$$

$$\Delta S^{\circ} = 1 \text{ mol} (173.26 \text{ J/K}\cdot\text{mol}) - [6 \text{ mol} (5.6 \text{ J/K}\cdot\text{mol}) + 3 \text{ mol} (130.7 \text{ J/K}\cdot\text{mol})] = -252.4 \text{ J/K}$$

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ} = 49.03 \text{ kJ} - (298 \text{ K})(-252.4 \text{ J/K})(1 \text{ kJ}/10^3 \text{ J}) = 124.3 \text{ kJ}$$

Reaction (a) is product-favored and enthalpy-driven.

Reaction (b) is enthalpy-driven.

19.26 (a) $\Delta G^{\circ}_{\text{rxn}} = \Delta G_f^{\circ}[\text{SO}_2(\text{g})] - \Delta G_f^{\circ}[\text{HgS}(s)]$

$$\Delta G^{\circ}_{\text{rxn}} = 1 \text{ mol} (-300.13 \text{ kJ/mol}) - 1 \text{ mol} (-50.6 \text{ kJ/mol}) = -249.5 \text{ kJ}$$

product-favored

(b) $\Delta G^{\circ}_{\text{rxn}} = 2 \Delta G_f^{\circ}[\text{H}_2\text{O}(g)] + 2 \Delta G_f^{\circ}[\text{SO}_2(g)] - 2 \Delta G_f^{\circ}[\text{H}_2\text{S}(g)]$

$$\Delta G^{\circ}_{\text{rxn}} = 2 \text{ mol} (-228.59 \text{ kJ/mol}) + 2 \text{ mol} (-300.13 \text{ kJ/mol}) - 2 \text{ mol} (-33.56 \text{ kJ/mol}) = -990.32 \text{ kJ}$$

product-favored

(c) $\Delta G^{\circ}_{\text{rxn}} = 2 \Delta G_f^{\circ}[\text{MgCl}_2(s)] - \Delta G_f^{\circ}[\text{SiCl}_4(g)]$

$$\Delta G^{\circ}_{\text{rxn}} = 2 \text{ mol} (-592.09 \text{ kJ/mol}) - 1 \text{ mol} (-622.76 \text{ kJ/mol}) = -561.42 \text{ kJ}$$

product favored

19.27 $\Delta G^\circ_{\text{rxn}} = \Delta G_f^\circ[\text{BaO(s)}] + \Delta G_f^\circ[\text{CO}_2(\text{g})] - \Delta G_f^\circ[\text{BaCO}_3(\text{s})]$
 $219.7 \text{ kJ} = 1 \text{ mol} (-520.38 \text{ kJ/mol}) + 1 \text{ mol} (-394.359 \text{ kJ/mol}) - 1 \text{ mol } \Delta G_f^\circ[\text{BaCO}_3(\text{s})]$
 $\Delta G_f^\circ[\text{BaCO}_3(\text{s})] = -1134.4 \text{ kJ/mol}$

19.32 $\text{CaSO}_4(\text{s}) \rightarrow \text{CaO(s)} + \text{SO}_3(\text{g})$
 $\Delta H^\circ = \Delta H_f^\circ[\text{CaO(s)}] + \Delta H_f^\circ[\text{SO}_3(\text{g})] - \Delta H_f^\circ[\text{CaSO}_4(\text{s})]$
 $\Delta H^\circ = 1 \text{ mol} (-635.09 \text{ kJ/mol}) + 1 \text{ mol} (-395.77 \text{ kJ/mol}) - 1 \text{ mol} (-1434.52 \text{ kJ/mol}) = 403.66 \text{ kJ}$
 $\Delta S^\circ = S^\circ[\text{CaO(s)}] + S^\circ[\text{SO}_3(\text{g})] - S^\circ[\text{CaSO}_4(\text{s})]$
 $\Delta S^\circ = 1 \text{ mol} (38.2 \text{ J/K}\cdot\text{mol}) + 1 \text{ mol} (256.77 \text{ J/K}\cdot\text{mol}) - 1 \text{ mol} (106.5 \text{ J/K}\cdot\text{mol}) = 188.5 \text{ J/K}$
 $\Delta G^\circ = 0 = \Delta H^\circ - T\Delta S^\circ = 403.66 \text{ kJ} - T(188.5 \text{ J/K})(1 \text{ kJ}/10^3 \text{ J})$
 $T = 2141 \text{ K}$ or greater

19.33 $\Delta G^\circ = -RT \ln K_p$
 $86.58 \text{ kJ/mol} = -(8.3145 \times 10^{-3} \text{ kJ/K}\cdot\text{mol})(298 \text{ K}) \ln K_p$
 $\ln K_p = -34.94$
 $K_p = 6.7 \times 10^{-16}$
 The large, positive ΔG° value results in a K_p value much less than 1

19.44 (a) $(\text{C}_2\text{H}_5)_2\text{O}(\ell) \leftrightarrow (\text{C}_2\text{H}_5)_2\text{O}(\text{g})$ At equilibrium, $\Delta G^\circ = 0$
 $\Delta S^\circ = \frac{\Delta H^\circ_{\text{vap}}}{T} = \frac{26.0 \times 10^3 \text{ J/mol}}{308.2 \text{ K}} = 84.4 \text{ J/K}\cdot\text{mol}$

(b) $(\text{C}_2\text{H}_5)_2\text{O}(\text{g}) \leftrightarrow (\text{C}_2\text{H}_5)_2\text{O}(\ell)$ $\Delta S^\circ = -84.4 \text{ J/K}\cdot\text{mol}$

19.50 At 897 °C the system is at equilibrium
 $\Delta G^\circ = -RT \ln K_p = -RT \ln (1.00) = 0$
 Assuming ΔH° values are relatively constant as the temperature changes,
 $\Delta S^\circ = \frac{\Delta H^\circ}{T} = \frac{179.1 \times 10^3 \text{ J/mol}}{1170 \text{ K}} = 153.1 \text{ J/K}\cdot\text{mol}$