Chapter 19
Principles of Reactivity: Entropy and Free Energy

Units for thermodynamic processes are typically expressed for the balanced equation given. Hence the equation for the formation of HCl: $H_2 + Cl_2 \rightarrow 2HCl$ has a $\Delta_rG°$, $\Delta_rH°$, and $\Delta_rS°$ that represent the formation of 2 mol of HCl. We can express this as "energy change"/mol-rxn, where "energy change" typically has units of kJ (for G,H) and J/K (for S). In this chapter, we shall omit the "mol-rxn" notation in the interest of brevity. *Unless otherwise noted*, answers should be read: $\Delta_rG°$ and $\Delta_rH°$, units will be **kJ/mol-rxn**, and for $\Delta_rS°$, units will be **J/K• mol-rxn**.

PRACTICING SKILLS

Entropy

1. Compound with the higher entropy:

    (a) CO_2 (s) at –78° vs **CO_2 (g) at 0 ˚C**: Entropy increases with temperature.

    (b) H_2O (ℓ) at 25 ˚C vs **H_2O (ℓ) at 50 ˚C**: Entropy increases with temperature.

    (c) Al_2O_3 (s) (pure) vs **Al_2O_3 (s) (ruby)**: Entropy of a solution (even a solid one) is greater than that of a pure substance.

    (d) **1 mol N_2 (g) at 1bar** vs 1 mol N_2 (g) at 10 bar: With the increased P, molecules have greater order.

3. Entropy changes:

    (a) KOH (s) $\rightarrow$ KOH(aq)

    $$\Delta_rS° \; = \; 91.6 \; \frac{J}{K•mol} (1 \text{ mol}) \quad - \; 78.9 \; \frac{J}{K•mol}(1 \text{ mol}) \quad = \; + 12.7 \; \frac{J}{K• \text{ mol-rxn}}$$

    The increase in entropy reflects the greater disorder of the solution state.
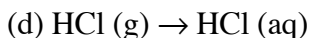
    (b) Na (g) $\rightarrow$ Na (s)

    $$\Delta_rS° \; = \; 51.21 \; \frac{J}{K•mol} (1 \text{ mol}) \quad - \; 153.765 \; \frac{J}{K•mol} (1 \text{ mol}) \quad = \; -102.55 \; \frac{J}{K• \text{ mol-rxn}}$$

    The lower entropy of the solid state is evidenced by the negative sign.

    (c) Br_2 (ℓ) $\rightarrow$ Br_2 (g)

    $$\Delta_rS° \; = 245.42 \; \frac{J}{K•mol} (1 \text{ mol}) \quad - \; 152.2 \; \frac{J}{K•mol}(1 \text{ mol}) \quad = \; + 93.2 \; \frac{J}{K• \text{ mol-rxn}}$$

   The increase in entropy is expected with the transition to the disordered state of a gas.

(d) $HCl (g) \rightarrow HCl (aq)$

$$\Delta_r S° = 56.5 \frac{J}{K•mol} (1 \text{ mol}) - 186.2 \frac{J}{K•mol} (1 \text{ mol}) = -129.7 \frac{J}{K• \text{ mol-rxn}}$$

The lowered entropy reflects the greater order of the solution state over the gaseous state.

5. Standard Entropy change for compound formation from elements:
    (a) HCl (g): $Cl_2 (g) + H_2 (g) \rightarrow 2 HCl (g)$
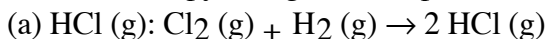
$$\Delta_r S° = 2 • S° HCl (g) - [1 • S° Cl_2 (g) + 1 • S° H_2 (g)]$$

$$= (2 \text{ mol})(186.2 \frac{J}{K•mol}) - [(1 \text{ mol})(223.08 \frac{J}{K•mol}) + (1 \text{ mol})(130.7 \frac{J}{K•mol})]$$

$$= + 18.6 \frac{J}{K} \text{ and } +9.3 \frac{J}{K• \text{ mol-rxn}}$$

(b) $Ca(OH)_2 (s)$: $Ca(s) + O_2 (g) + H_2 (g) \rightarrow Ca(OH)_2 (s)$
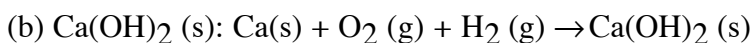
$$\Delta_r S° = 1 • S° Ca(OH)_2 (s) - [1 • S° Ca (s) +1 • S° O_2 (g) + 1 • S° H_2 (g)]$$

$$= (1 \text{ mol})(83.39 \frac{J}{K•mol}) - [(1 \text{ mol})(41.59 \frac{J}{K•mol}) + (1 \text{ mol})(205.07 \frac{J}{K•mol}) +$$

$$(1 \text{ mol})(130.7 \frac{J}{K•mol})]$$

$$= -293.97 \frac{J}{K• \text{ mol-rxn}} \text{ (or } -294.0 \frac{J}{K• \text{ mol-rxn}} \text{ to 4 sf)}$$

7. Standard molar entropy changes for:

    (a) $2 Al (s) + 3 Cl_2 (g) \rightarrow 2 AlCl_3 (s)$
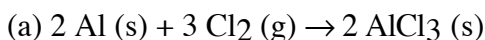
$$\Delta_r S° = 2 • S° AlCl_3 (s) - [2 • S° Al (s) + 3 • S° Cl_2 (g)]$$

$$= (2 \text{ mol})(109.29 \frac{J}{K•mol}) - [(2 \text{ mol})(28.3 \frac{J}{K•mol}) + (3 \text{ mol})(223.08 \frac{J}{K•mol})]$$

$$= -507.3 \frac{J}{K• \text{ mol-rxn}}$$

    (b) $2 CH_3OH (\ell) + 3 O_2 (g) \rightarrow 2 CO_2 (g) + 4 H_2O (g)$
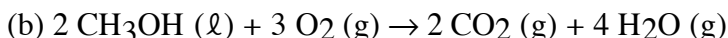
$$\Delta_r S° = [2 • S° CO_2 (g) + 4 • S° H_2O (g)] - [2 • S° CH_3OH (\ell) + 3 • S° O_2 (g)]$$

$$= [(2 \text{ mol})(213.74 \frac{J}{K•mol}) + (4 \text{ mol})(188.84 \frac{J}{K•mol})] -$$

$$[(2 \text{ mol})(127.19 \frac{J}{K•mol}) + (3 \text{ mol})(205.07 \frac{J}{K•mol})]$$

$$= + 313.25 \frac{J}{K• \text{ mol-rxn}}$$

In (a) we see the sign of $\Delta_r S°$ as negative—expected since the reaction results in the decrease in the number of moles of gas. In (b), the sign of is positive—as expected, since the reaction produces a larger number of moles of gaseous products than gaseous reactants.

$\Delta_r S°$(universe) and Spontaneity

9. Is the reaction: Si (s) + 2 Cl$_2$ (g) → SiCl$_4$ (g) spontaneous?

$\Delta_r S°$ (system) = 1 • S° SiCl$_4$ (g) - [1 • S° Si (s) + 2 • S° Cl$_2$ (g)]

= (1 mol)(330.86 $\frac{J}{K \cdot mol}$) - [(1 mol)(18.82 $\frac{J}{K \cdot mol}$)+ (2 mol)(223.08 $\frac{J}{K \cdot mol}$)]

= -134.12 $\frac{J}{K \cdot mol\text{-}rxn}$

To calculate $\Delta_r S°$ (surroundings), we calculate $\Delta H°$(system):

$\Delta H°$ = 1 • $\Delta H°$ SiCl$_4$ (g) - [1 • $\Delta H°$ Si (s) + 2 • $\Delta H°$ Cl$_2$ (g)]

= (1 mol)(- 662.75 $\frac{kJ}{mol}$) - [(1 mol)(0 $\frac{kJ}{mol}$)+ (2 mol)(0 $\frac{kJ}{mol}$)] = -662.75 $\frac{kJ}{mol\text{-}rxn}$

$\Delta_r S°$ (surroundings) = - $\Delta H°$/T = (662.75 x 10^3 J/mol)/298.15 K = 2222.9 $\frac{J}{K \cdot mol\text{-}rxn}$

$\Delta_r S°$ (universe) = $\Delta_r S°$ (system) + $\Delta_r S°$ (surroundings) =

(-134.12 + 2222.9) = 2088.7 $\frac{J}{K \cdot mol\text{-}rxn}$

11. Is the reaction: 2 H$_2$O(ℓ) → 2 H$_2$ (g) + O$_2$ (g) spontaneous?

$\Delta_r S°$ (system) = [2 • S° H$_2$ (g) + 1 • S° O$_2$ (g)] - 2 • S° H$_2$O (ℓ)

= [(2 mol)(130.7 $\frac{J}{K \cdot mol}$) +(1 mol)(205.07 $\frac{J}{K \cdot mol}$)] - (2 mol)(69.95 $\frac{J}{K \cdot mol}$)

= +326.57 $\frac{J}{K}$ and for decomposition of 1 mol of water: +326.57/2 =

163.3 $\frac{J}{K \cdot mol\text{-}rxn}$

To calculate $\Delta_r S°$ (surroundings), we calculate $\Delta H°$(system):

$\Delta H°$(system) = [2 • $\Delta H°$ H$_2$ (g) + 1 • $\Delta H°$ O$_2$ (g)] - 2 • $\Delta H°$ H$_2$O (ℓ)

= [(2 mol)(0 $\frac{kJ}{mol}$) +(1 mol)(0 $\frac{kJ}{mol}$)] - (2 mol)(-285.83 $\frac{kJ}{mol}$)

$= +571.66 \dfrac{kJ}{mol}$ and for decomposition of 1 mol of water: $+571.66/2 = 285.83 \dfrac{kJ}{\text{mol-rxn}}$

$\Delta_r S°$ (surroundings) $= - \Delta H°/T = -(285.83 \times 10^3 \text{ J/mol})/298.15 \text{ K} = - 958.68 \dfrac{J}{K\bullet \text{mol-rxn}}$

$\Delta_r S°$ (universe) $= \Delta_r S°$ (system) $+ \Delta_r S°$ (surroundings) $= 163.3 + - 958.68$

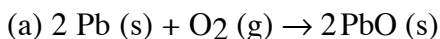$= -795.4 \dfrac{J}{K\bullet \text{mol-rxn}}$ Since this value is less than zero, the process is not spontaneous.

13. Using Table 19.2 classify each of the reactions:

   (a) $\Delta H°_{system} = -$, $\Delta_r S°_{system} = -$ Product-favored at lower T

   (b) $\Delta H°_{system} = +$, $\Delta_r S°_{system} = -$ Not product-favored under any conditions

Gibbs Free Energy

15. Calculate $\Delta_r G°$ for :

   (a) 2 Pb (s) + O_2 (g) → 2 PbO (s)

   $\Delta_r H°= (2 \text{ mol})(-219 \dfrac{kJ}{mol}$) $- [0 + 0] = -438$ kJ

   $\Delta_r S° = (2 \text{ mol})(66.5 \dfrac{J}{K\bullet mol}$) $-$

   $[(2 \text{ mol})(64.81 \dfrac{J}{K\bullet mol}$) $+ (1 \text{ mol})(205.07 \dfrac{J}{K\bullet mol}$)] $= -201.7$ J/K

   $\Delta_r G° = \Delta_r H° - T\Delta_r S°$

   $= - 438 \text{ kJ} - (298.15 \text{ K})(-201.7 \text{ J/K})(\dfrac{1.000 \text{ kJ}}{1000. \text{ J}}$) $= - 378$ kJ

   Reaction is product-favored since $\Delta G < 0$. With the very large negative ΔH, the process is enthalpy driven.

   (b) NH_3(g) + HNO_3(aq) → NH_4NO_3 (aq)
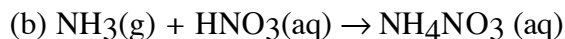
   $\Delta_r H°= (1 \text{ mol})(-339.87 \dfrac{kJ}{mol})$ - $[(1 \text{ mol})(-45.90 \dfrac{kJ}{mol})+(1 \text{ mol})(-207.36 \dfrac{kJ}{mol}] = -86.61$ kJ

   $\Delta_r S° = (1 \text{ mol})(259.8 \dfrac{J}{K\bullet mol}$) $-$

   $[(1 \text{ mol})(192.77 \dfrac{J}{K\bullet mol}$) $+ (1 \text{ mol})(146.4 \dfrac{J}{K\bullet mol}$)] $= -79.4 \dfrac{J}{K\bullet \text{mol-rxn}}$

   $\Delta rG°= \Delta_r H° - T\Delta_r S° = -86.61 \text{ kJ} - (298.15 \text{ K})(-79.4 \text{ J/K})(\dfrac{1.000 \text{ kJ}}{1000. \text{ J}}) = -62.9 \dfrac{kJ}{\text{mol-rxn}}$

Reaction is product-favored since $\Delta G < 0$. With the very large negative ΔH, the process is enthalpy driven.

17. Calculate the molar free energies of formation for:
    (a) CS_2 (g) The reaction is: C (graphite) + 2 S (s,rhombic) $\rightarrow$ CS_2 (g)

$$\Delta_r H° = (1 \text{ mol})(116.7 \frac{kJ}{mol}) - [0 + 0] = +116.7 \text{ kJ}$$

$$\Delta_r S° = (1 \text{ mol})(237.8 \frac{J}{K \cdot mol}) - [(1 \text{ mol})(5.6 \frac{J}{K \cdot mol}) + (2 \text{ mol})(32.1 \frac{J}{K \cdot mol})]$$

$$= +168.0 \text{ J/K}$$

$$\Delta_f G° = \Delta_f H° - T\Delta_r S° = (116.7 \text{ kJ}) - (298.15 \text{ K})(168.0 \frac{J}{K})(\frac{1.000 \text{ kJ}}{1000 \text{ J}})$$

$$= + 66.6 \text{ kJ} \qquad \text{Appendix value: 66.61 kJ/mol}$$

(b) NaOH (s)   The reaction is: Na (s) + $\frac{1}{2}$ O_2(g) + $\frac{1}{2}$ H_2(g) $\rightarrow$ NaOH (s)

$$\Delta_r H° = (1 \text{ mol})(-425.93 \frac{kJ}{mol}) - [0 + 0 + 0] = -425.93 \frac{kJ}{mol\text{-}rxn}$$

$$\Delta_r S° = (1 \text{ mol})(64.46 \frac{J}{K \cdot mol}) -$$

$$[(1 \text{ mol})(51.21 \frac{J}{K \cdot mol}) + (\frac{1}{2} \text{ mol})(205.07 \frac{J}{K \cdot mol}) + (\frac{1}{2} \text{ mol})(130.7 \frac{J}{K \cdot mol})]$$

$$= -154.6 \frac{J}{K \cdot mol\text{-}rxn}$$

$$\Delta_r G° = \Delta_r H° - T\Delta_r S° = (-425.93 \text{ kJ}) - (298.15 \text{ K})(-154.6 \text{ J/K})(\frac{1.000 \text{ kJ}}{1000. \text{ J}})$$

$$= -379.82 \text{ kJ} \qquad \text{Appendix value: -379.75 kJ/mol}$$

(c) ICl (g) The reaction is: $\frac{1}{2}$ I_2 (g) + $\frac{1}{2}$ Cl_2 (g) $\rightarrow$ ICl (g)

$$\Delta_r H° = (1 \text{ mol})(+17.51 \frac{kJ}{mol}) - [0 + 0] = +17.51 \frac{kJ}{mol\text{-}rxn}$$

$$\Delta_r S° = (1 \text{ mol})(247.56 \frac{J}{K \cdot mol}) -$$

$$[(\frac{1}{2} \text{mol})(116.135 \frac{J}{K \cdot mol}) + (\frac{1}{2} \text{ mol})(223.08 \frac{J}{K \cdot mol})]$$

$$= +77.95 \frac{J}{K \cdot mol\text{-}rxn} \text{ J/K}$$

$$\Delta_r G° = \Delta_r H° - T\Delta_r S° = (+17.51 \text{ kJ}) - (298.15 \text{ K})(+77.95 \text{ J/K})(\frac{1.000 \text{ kJ}}{1000. \text{ J}})$$

$$= -5.73 \text{ kJ} \qquad\qquad \text{Appendix value: } -5.73 \text{ kJ/mol}$$

Free Energy of Formation

19. Calculate $\Delta_r G°$ for the following equations. Are they product-favored?

(a) $2 \text{ K (s)} + Cl_2 \text{ (g)} \rightarrow 2 \text{ KCl (s)}$
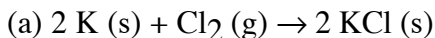
$\Delta_r G° = [2 \cdot \Delta_f G° \text{ KCl(s)}] - [1 \cdot \Delta_f G° \text{ } Cl_2(g) + 2 \cdot \Delta_f G° \text{ K (s)}]$

$$= [(2 \text{ mol})(-408.77 \frac{\text{kJ}}{\text{mol}}] - [(1 \text{ mol})(0 \frac{\text{kJ}}{\text{mol}}) + (2 \text{ mol})(0 \frac{\text{kJ}}{\text{mol}})]$$

$$= -817.54 \text{ kJ}$$

With a $\Delta G < 0$, the reaction is product-favored.

(b) $2 \text{ CuO (s)} \rightarrow 2 \text{ Cu (s)} + O_2 \text{ (g)}$

$\Delta_r G° = [2 \cdot \Delta_f G° Cu(s) + \Delta_f G° O_2 \text{ (g)}] - [2 \cdot \Delta_f G° \text{ CuO (s)}]$
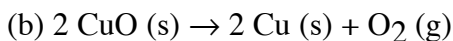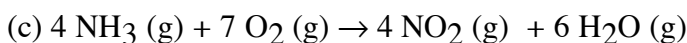
$$\Delta_r G° = [(2 \text{ mol})(0 \frac{\text{kJ}}{\text{mol}}) + (1 \text{ mol})(0 \frac{\text{kJ}}{\text{mol}})] - [(2\text{mol})(-128.3 \frac{\text{kJ}}{\text{mol}})$$

$$= +256.6 \text{ kJ}$$

With a $\Delta G > 0$, the reaction is not product-favored.

(c) $4 \text{ NH}_3 \text{ (g)} + 7 \text{ } O_2 \text{ (g)} \rightarrow 4 \text{ NO}_2 \text{ (g)} + 6 \text{ } H_2O \text{ (g)}$

$\Delta_r G° = [4 \cdot \Delta G°_f \text{ NO}_2 \text{ (g)} + 6 \cdot \Delta G°_f \text{ } H_2O \text{ (g)}] - [4 \cdot \Delta G°_f \text{ NH}_3 \text{ (g)} + 7 \cdot \Delta G°_f \text{ } O_2 \text{ (g)}]$

$$\Delta_r G° = [(4\text{mol})(+51.23 \frac{\text{kJ}}{\text{mol}}) + (6 \text{ mol})(-228.59 \frac{\text{kJ}}{\text{mol}}] -$$

$$[(4 \text{ mol})(-16.37 \frac{\text{kJ}}{\text{mol}}) + (7 \text{ mol})(0 \frac{\text{kJ}}{\text{mol}})] = -1101.14 \text{ kJ}$$

With a $\Delta G < 0$, the reaction is product-favored.

21. Value for $\Delta_f G°$ of $BaCO_3(s)$:

$\Delta_r G° = [\Delta_f G° \text{ BaO(s)} + \Delta_f G° \text{ } CO_2(g)] - [\Delta_f G° \text{ } BaCO_3(s)]$

$$+219.7 \text{ kJ} = [(1 \text{ mol})(-520.38 \frac{\text{kJ}}{\text{mol}}) + (1 \text{ mol})(-394.359 \frac{\text{kJ}}{\text{mol}})] - \Delta G°_f \text{ } BaCO_3(s)$$

$+219.7 \text{ kJ} = -914.74 \text{ kJ} - \Delta_f G° \text{ } BaCO_3(s)$

$-1134.4 \text{ kJ/mol} = +\Delta_f G° \text{ } BaCO_3(s)$

Effect of Temperature on ΔG

23. Entropy-favored or Enthalpy-favored reactions?

(a) N_2 (g) + 2 O_2 (g) $\rightarrow$ 2 NO_2 (g)
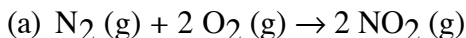
$$\Delta_r H° = (2 \text{ mol})(+33.1 \frac{kJ}{mol}) - [0 + 0] = +66.2 \frac{kJ}{mol\text{-}rxn}$$

$$\Delta_r S° = (2 \text{ mol})(+240.04 \frac{J}{K \bullet mol}) -$$

$$[(1 mol)(191.56 \frac{J}{K \bullet mol}) + (2 \text{ mol})(+205.07 \frac{J}{K \bullet mol})] = -121.62 \frac{J}{K \bullet mol\text{-}rxn}$$

$$\Delta_r G° = (2 \text{ mol})(51.23 \frac{kJ}{mol}) - [(1 \text{ mol})(0 \frac{kJ}{mol}) + (1 \text{ mol})(0 \frac{kJ}{mol})] = 102.5 \text{ kJ}$$

The reaction is **not** entropy OR enthalpy favored. There is **no** T at which ΔG < 0.

(b) 2 C (s) + O_2 (g) $\rightarrow$ 2 CO (g)

$$\Delta_r H° = (2 \text{ mol})(-110.525 \frac{kJ}{mol}) - [0 + 0] = -221.05 \frac{kJ}{mol\text{-}rxn}$$

$$\Delta_r S° = (2 \text{ mol})(+197.674 \frac{J}{K \bullet mol}) -$$

$$[(2 \text{ mol})(+5.6 \frac{J}{K \bullet mol}) + (1 mol)(+205.07 \frac{J}{K \bullet mol})] = +179.1 \frac{J}{K \bullet mol\text{-}rxn}$$

$$\Delta_r G° = (2 \text{ mol})(-137.168 \frac{kJ}{mol}) - [(1 \text{ mol})(0 \frac{kJ}{mol}) + (1 \text{ mol})(0 \frac{kJ}{mol})]$$

$$= -274.336 \text{ kJ}$$

This reaction is **both** entropy- and enthalpy-favored *at all temperatures*.

(c) CaO (s) + CO_2 (g) $\rightarrow$ $CaCO_3$ (s)
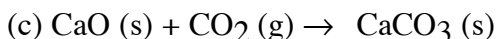
$$\Delta_r H° = (1 \text{ mol})(-1207.6 \frac{kJ}{mol}) - [(1 mol)(-635.0 \frac{kJ}{mol}) + (1 mol)(-393.509 \frac{kJ}{mol})]$$

$$= -179.0 \frac{kJ}{mol\text{-}rxn}$$

$$\Delta_r S° = (1 \text{ mol})(+91.7 \frac{J}{K \bullet mol}) -$$

$$[(1 mol)(38.2 \frac{J}{K \bullet mol}) + (1 mol)(+213.74 \frac{J}{K \bullet mol})] = -160.2 \frac{J}{K \bullet mol\text{-}rxn}$$

$$\Delta_r G° = (1 \text{ mol})(-1129.16 \frac{\text{kJ}}{\text{mol}}) \ -$$

$$[(1\text{mol})(-603.42 \frac{\text{kJ}}{\text{mol}}) + (1\text{mol})(-394.359 \frac{\text{kJ}}{\text{mol}})] = -131.4 \frac{\text{kJ}}{\text{mol-rxn}}$$
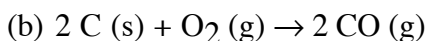
This reaction is *enthalpy-favored* and will be spontaneous at low temperatures.

(d) 2 NaCl (s) $\rightarrow$ 2 Na (s) + Cl$_2$ (g)

$$\Delta_r H° = [(2 \text{ mol})(0 \frac{\text{kJ}}{\text{mol}}) + (1\text{mol})(0 \frac{\text{kJ}}{\text{mol}})] - (2\text{mol})(-411.12 \frac{\text{kJ}}{\text{mol}})] = + 822.24 \frac{\text{kJ}}{\text{mol-rxn}}$$

$$\Delta_r S° = [(2 \text{ mol})(+51.21 \frac{\text{J}}{\text{K} \bullet \text{mol}}) + (1\text{mol})(+223.08 \frac{\text{J}}{\text{K} \bullet \text{mol}})] \ -$$

$$(2\text{mol})(+72.11 \frac{\text{J}}{\text{K} \bullet \text{mol}})] = + 181.28 \frac{\text{J}}{\text{K} \bullet \text{mol-rxn}}$$

$$\Delta_r G° = [(2 \text{ mol})(0 \frac{\text{kJ}}{\text{mol}}) + (1\text{mol})(0 \frac{\text{kJ}}{\text{mol}})] - (2\text{mol})(-384.04 \frac{\text{kJ}}{\text{mol}})] = +768.08 \frac{\text{kJ}}{\text{mol-rxn}}$$

This reaction is *entropy-favored* and will be spontaneous at high temperatures.

25. For the decomposition of MgCO$_3$ (s) $\rightarrow$ MgO (s) + CO$_2$ (g):

(a) $\Delta_r S°$(system) = [1 • S° MgO (s) + 1 • S° CO$_2$ (g)] - 1 • S° MgCO$_3$ (s)

$$= [(1\text{mol})(26.85 \frac{\text{J}}{\text{K}\bullet\text{mol}}) + (1\text{mol})(213.74 \frac{\text{J}}{\text{K}\bullet\text{mol}})] - (1\text{mol})(65.84 \frac{\text{J}}{\text{K}\bullet\text{mol}})$$

$$= +174.75 \frac{\text{J}}{\text{K}\bullet \text{mol-rxn}}$$

Calculate $\Delta H°$(system):

$\Delta H°$(system) = [1 • $\Delta H°$ MgO (s) + 1 • $\Delta H°$ CO$_2$ (g)] - 1 • $\Delta H°$ MgCO$_3$ (s)

$$= [(1 \text{ mol})(-601.24 \frac{\text{kJ}}{\text{mol}}) + (1 \text{ mol})(-393.509 \frac{\text{kJ}}{\text{mol}})] - (1 \text{ mol})(-1111.69 \frac{\text{kJ}}{\text{mol}})$$
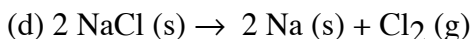
$$= +116.94 \frac{\text{kJ}}{\text{mol-rxn}}$$

(b) $\Delta_r G°$ = - $\Delta H°$ - T • S° = +116.94 $\frac{\text{kJ}}{\text{mol-rxn}}$ - (298 K)(+174.75 $\frac{\text{J}}{\text{K}\bullet \text{mol-rxn}}$)($\frac{1 \text{ kJ}}{1000 \text{ J}}$) =

$$= +64.87 \frac{\text{kJ}}{\text{mol-rxn}} \text{ , so not spontaneous at 298 K}$$

(c) From Table 19.2 we observe that this type of reaction (ΔH = + and $\Delta_r S$ = +) is

spontaneous at higher T (product-favored).

Free Energy and Equilibrium Constants

27. Calculate K_p for the reaction:

$$\frac{1}{2} N_2(g) + \frac{1}{2} O_2(g) \rightarrow NO\ (g) \qquad \Delta_rG° = + 86.58\ kJ/mol\ NO$$
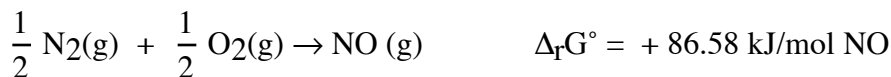
$\Delta_rG° = -RT \ln K_p$ so $86.58 \times 10^3\ J/mol = - (8.3145\ \frac{J}{K \cdot mol})(298.15\ K) \ln K_p$

$-34.926 = \ln K_p$ and $6.8 \times 10^{-16} = K_p$

Note that the + value of $\Delta_rG°$ results in a value of K_p which is small--reactants are favored. A negative value would result in a large K_p -- a process in which the products were favored.

29. From the $\Delta G°$ and K_p, determine if the hydrogenation of ethylene is product-favored:

Using $\Delta_fG°$ data from the Appendix: C_2H_4 (g) + H_2 (g) $\rightarrow C_2H_6$ (g)

$\Delta_rG° = (1\ mol)(-31.89\ \frac{kJ}{mol}) - [(1mol)(68.35\ \frac{kJ}{mol}) + (1mol)(0\ \frac{kJ}{mol})] = -100.24\ kJ$
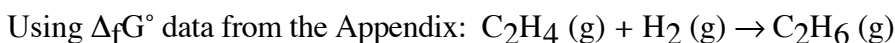
and since $\Delta_rG° = -RT \ln K_p$

$-100.24 \times 10^3\ J/mol = - (8.3145\ \frac{J}{K \cdot mol})(298.15\ K) \ln K_p$

$40.436 = \ln K_p$ and $K_p = 3.64 \times 10^{17}$

The negative value of ΔG means the reaction is product-favored. The large value of ΔG means that Kp is very large.

General Questions

31. Compound with higher standard entropy:
    (a) HF (g) vs HCl (g) vs **HBr (g)**: Entropy increases with molecular size (mass)
    (b) NH_4Cl (s) vs **NH_4Cl (aq)**: Entropy of solutions is greater than that of the solid.
    (c) N_2 (g) vs **C_2H_4 (g)**: Entropy increases with molecular complexity
    (d) NaCl(s) vs **NaCl (g)**: Entropy of the gaseous state is very high. The solid state has lower entropy.

33. For the reaction C_6H_6 (ℓ) + 3 H_2(g) $\rightarrow C_6H_{12}$(ℓ), $\Delta_rH° = - 206.7\ kJ$, and $\Delta_rS° = -361.5\ J/K$

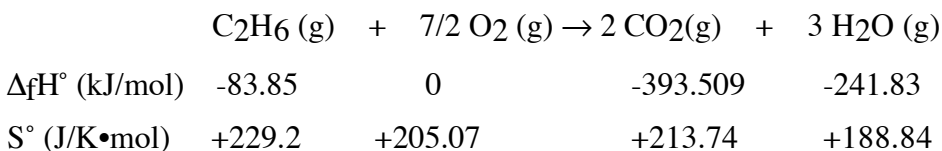   Is the reaction spontaneous under standard conditions? Calculating $\Delta G°$ will answer this question.

    $\Delta_rG° = \Delta_rH° - T\Delta_rS°$

$$= -206.7 \text{ kJ} - (298.15 \text{ K})(-361.5 \ \frac{J}{K})(\ \frac{1.000 \text{ kJ}}{1000 \text{ J}}) = \quad \text{kJ}$$

$$= -206.7 \text{ kJ} - (-107.8 \text{ kJ}) = -98.9 \ \frac{\text{kJ}}{\text{mol-rxn}}$$

The negative value for $\Delta_r G°$ tells us that the reaction would be spontaneous (product-favored) under standard conditions. The negative value for $\Delta_r H°$ tells us that the reaction is enthalpy-driven.

35. Calculate $\Delta_r H°$ and $\Delta_r S°$ for the combustion of ethane:

$$C_2H_6 \text{ (g)} \quad + \quad 7/2 \ O_2 \text{ (g)} \rightarrow 2 \ CO_2\text{(g)} \quad + \quad 3 \ H_2O \text{ (g)}$$

$\Delta_f H°$ (kJ/mol) -83.85	0	-393.509	-241.83
$S°$ (J/K•mol) +229.2	+205.07	+213.74	+188.84

$\Delta_r H° = [2 \bullet \Delta H°_f \ CO_2\text{(g)} + 3 \bullet \Delta H°_f \ H_2O \text{ (g)}] - [1 \bullet \Delta H°_f \ C_2H_6 \text{ (g)} + 7/2 \bullet \Delta H°_f \ O_2 \text{ (g)}]$

$$= [(2\text{mol})(-393.509 \ \frac{\text{kJ}}{\text{mol}}) + (3\text{mol})(-241.83 \ \frac{\text{kJ}}{\text{mol}})] - [(1\text{mol})(-83.85 \text{ kJ/mol}) + 0]$$

$$= -1428.66 \ \frac{\text{kJ}}{\text{mol-rxn}}$$

$\Delta_r S° = [2 \bullet S° \ CO_2\text{(g)} + 3 \bullet S° \ H_2O \text{ (g)}] - [1 \bullet S° \ C_2H_6 \text{ (g)} + 7/2 \bullet S° \ O_2 \text{ (g)}]$

$$= [(2 \text{ mol})(213.74 \ \frac{J}{K \bullet \text{mol}}) + (3 \text{ mol})(188.84 \ \frac{J}{K \bullet \text{mol}})] -$$

$$[(1 \text{ mol})(229.2 \ \frac{J}{K \bullet \text{mol}}) + (7/2 \text{ mol})(205.07 \ \frac{J}{K \bullet \text{mol}})] = +47.1 \ \frac{J}{K \bullet \text{ mol-rxn}}$$

$\Delta_r S°\text{(surroundings)} \qquad = \frac{-\Delta H_{\text{rxn}}}{T}$ (Assuming we're at 298 K)

$$= \frac{1428.66 \text{ kJ}}{298.15 \text{ K}} \bullet \frac{1000 \text{ J}}{1 \text{ kJ}} \quad = 4791.7 \text{ J/K}$$

so $\Delta_r S°\text{(system)} + \Delta_r S°\text{(surroundings)} \quad = \quad +47.1 \text{ J/K} + 4791.7 \text{ J/K}$

$$= \quad 4838.8 \text{ J/K} \text{ or } +4840 \ \frac{J}{K \bullet \text{ mol-rxn}} \text{ (3 sf)}$$

Since $\Delta_r H° = -$ and $\Delta_r S° = +$, the process is product-favored.

This calculation is consistent with our expectations. We know that hydrocarbons burn completely (in the presence of sufficient oxygen) to produce carbon dioxide and water.

37. (a) Calculate $\Delta_r G°$ for NH_3 (g) + HCl (g)   → NH_4Cl (s)

S° (J/K•mol)	192.77	186.2	94.85
$\Delta_f H°$ (kJ/mol)	– 45.90	- 92.31	- 314..55

$\Delta_r S°$ = 1 • S° NH_4Cl (s) - [1 • S° NH_3 (g) + 1 • S° HCl (g)]

$\quad\quad$ = (1 mol)(94.85 J/K • mol) - [(1 mol)(192.77 J/K • mol) +

$\quad\quad\quad\quad\quad\quad\quad\quad\quad$ (1 mol)(186.2 J/K • mol)] = - 284.1 J/K

$\Delta_r H°$ = 1 • $\Delta_f H°$ NH_4Cl (s) - [1 • $\Delta_f H°NH_3$ (g) + 1 • $\Delta_f H°$ HCl (g)]

$\quad\quad$ = (1 mol)(- 314.55 kJ/mol) - [(1 mol)(- 45.90 kJ/mol) + (1 mol)(- 92.3l kJ/mol)]

$\quad\quad$ = - 176.34 kJ

$\Delta_r G° = \Delta_r H°$ - T $\Delta_r S°$

$\quad\quad$ = - 176.34 kJ - (298.15 K)(- 284.1 J/K)$(\dfrac{1.000\ kJ}{1000\ J}$)

$\quad\quad$ = - 176.01 + 84.67 = - 91.64 $\dfrac{kJ}{mol\text{-}rxn}$

$\Delta_r S°$(surroundings) $= \dfrac{-\Delta_r H}{T}$ (Assuming we're at 298 K)

$\quad\quad\quad$ $= \dfrac{176.34\ kJ}{298.15\ K}$ • $\dfrac{1000\ J}{1\ kJ}$ = 591.45 J/K

so $\Delta_r S°$(system) + $\Delta_r S°$(surroundings) = -284.12 J/K + 591.45 J/K = +307.3 $\dfrac{J}{K• mol\text{-}rxn}$

The value for $\Delta_r G°$ for the equation is negative, indicating that is product-favored. The reaction is enthalpy driven (Δ_r H < 0).

(b) Calculate K_p for the reaction:

$\Delta_r G°$= - RT ln K_p so -91.64 x 10^3 J/mol =   - (8.3145 $\dfrac{J}{K • mol}$)(298.15 K) ln K_p

36.97 = ln K_p and 1.13 x 10^{16} = K_p

39. Calculate K_p for the formation of methanol from its' elements:

Begin by calculating a $\Delta_r G°$

$\Delta_r G° = \Delta_f G_{CH3OH}(ℓ) - [\Delta_f G_{C(graphite)} +1/2 •\Delta_f G_{O2(g)} + 2 • \Delta_f G_{H2(g)}]$

$\Delta_r G°$ = -166.14 kJ – (0 kJ + 0 kJ + 0 kJ) = -166.14 kJ

$\Delta_r G°$ = - RT ln K_p

-166.1 x 10^3 J/mol =   - (8.3145 $\dfrac{J}{K • mol}$)(298.15 K) ln K_p

$67.00 = \ln K_p$ and $1.3 \times 10^{29} = K_p$

The large value of K_p indicates that this process is product-favored at 298 K. Judging by the relative numbers of gaseous particles, (without doing a calculation), one can see that ΔrS for the reaction is < 0, so higher temperatures would reduce the value of K_p.

Regarding the connection between $\Delta G°$ and K, the more negative the value of $\Delta G°$, the larger the value of K.

41. Calculate the $\Delta_r S°$ for the vaporization of ethanol at 78.0 °C.

The $\Delta_r S = \dfrac{\Delta_{vap}H}{T} = \dfrac{39.3 \times 10^3 \text{ J}}{351 \text{ K}} = 112 \dfrac{\text{J}}{\text{K} \cdot \text{mol-rxn}}$

43. For the decomposition of phosgene:

$\Delta_r H° = [\Delta_f H°CO \text{ (g)} + \Delta_f H° Cl_2 \text{ (g)}] - [\Delta_f H° \; COCl_2(g)]$

$\Delta_r H° = [(1 \text{ mol.})(-110.525 \dfrac{\text{kJ}}{\text{mol}}) + (1\text{mol})(0 \dfrac{\text{kJ}}{\text{mol}})] - [(1 \text{ mol})(-218.8 \dfrac{\text{kJ}}{\text{mol}})] = 108.275 \dfrac{\text{kJ}}{\text{mol}}$

$\Delta_r S° = [S° \; CO \text{ (g)} + S° \; Cl_2 \text{ (g)}] - [S° \; COCl_2(g)]$

$\Delta_r S° = [(1 \text{ mol})(197.674 \dfrac{\text{J}}{\text{K} \cdot \text{mol}}) + (1 \text{ mol})(223.07 \dfrac{\text{J}}{\text{K} \cdot \text{mol}})] -$

$[(1 \text{ mol})(283.53 \dfrac{\text{J}}{\text{K} \cdot \text{mol}})] = 137.2 \dfrac{\text{J}}{\text{K} \cdot \text{mol-rxn}}$

Using the $\Delta_r S$ data, we can see that raising the temperature will favor the endothermic decomposition of this substance.

45. For the reaction of sodium with water: Na (s) + $H_2O(\ell) \rightarrow$ NaOH(aq) + $\dfrac{1}{2}$ H_2 (g)

Predict signs for $\Delta_r H°$ and $\Delta_r S°$:
This one seems easy! The reaction of sodium with water gives off heat, and the heat frequently ignites the hydrogen gas that is concomitantly evolved. $\Delta_r H° = $ **-**.

Regarding entropy, the system changes from one with a solid (low entropy) and a liquid (higher entropy) to a solution (*frequently* higher entropy than liquid) and a gas (high entropy). So we would predict that the entropy would increase, i.e. $\Delta_r S° = $ **+**.

Now for the calculation:

$\Delta_r H° = [1 \bullet \Delta_f H° \; NaOH(aq) + \dfrac{1}{2} \bullet \Delta_f H°H_2(g)] - [1 \bullet \Delta_f H° \; Na(s) + 1 \bullet \Delta_f H° \; H_2O(\ell)]$

$= [(1 \text{ mol})(-469.15 \dfrac{\text{kJ}}{\text{mol}}) + (\dfrac{1}{2}\text{mol})(0)] - [(1 \text{ mol})(0) + (1 \text{ mol})(-285.83 \dfrac{\text{kJ}}{\text{mol}})]$

$$= -183.32 \frac{kJ}{mol\text{-}rxn}$$

$$\Delta_r S° = [1 \cdot S° \, NaOH(aq) + \frac{1}{2} \cdot S° \, H_2(g)] - [1 \cdot S° \, Na(s) + 1 \cdot S° \, H_2O(\ell)]$$

$$= [(1 \; mol)(48.1 \frac{J}{K \cdot mol}) + (\frac{1}{2} \; mol)(130.7 \frac{J}{K \cdot mol})] -$$

$$[(1 \; mol)(51.21 \frac{J}{K \cdot mol}) + (1 \; mol)(69.95 \frac{J}{K \cdot mol})]$$

$$= -7.7 \frac{J}{K \cdot mol\text{-}rxn}$$

As expected, the $\Delta_r H°$ for the reaction is negative! The surprise comes in the calculation for $\Delta_r S°$. While we anticipate the sign to be positive, we find a slightly negative number—reflecting the order (hence a decrease in entropy) that can occur as solutions occur.

47. For the reaction : $BCl_3(g) + 3/2 \; H_2(g) \rightarrow B(s) + \; 3HCl(g)$

$$S° (\frac{J}{K \cdot mol}) \quad 290.17 \qquad 130.7 \quad 5.86 \qquad 186.2$$

$$\Delta_f H° (\frac{kJ}{mol}) \quad -402.96 \qquad 0 \qquad 0 \qquad -92.31$$

$$\Delta_r H° = [3 \cdot \Delta_f H° \, HCl(g) + 1 \cdot \Delta_f H° \, B(s)] - [1 \cdot \Delta_f H° \, BCl_3(g) + 3/2 \, \Delta_f H° \, H_2(g)]$$

$$\Delta_r H° = [(3 \; mol)(-92.31 \frac{kJ}{mol}) + (1 \; mol)(0)] - [(1 \; mol)(-402.96 \frac{kJ}{mol}) + (3/2 \; mol)(0)]$$

$$= 126.03 \frac{kJ}{mol\text{-}rxn}$$

$$\Delta_r S° = [3 \cdot S° \, HCl(g) + 1 \cdot S° \, B(s)] - [1 \cdot S° \, BCl_3(g) + 3/2 \, S° \, H_2(g)]$$

$$\Delta_r S° = [(3 \; mol)(186.2 \frac{J}{K \cdot mol}) + (1 \; mol)(5.86 \frac{J}{K \cdot mol})] - [(1 mol)(290.17 \frac{J}{K \cdot mol})$$

$$+ (3/2 \; mol)(130.7 \frac{J}{K \cdot mol})] = 78.2 \frac{J}{K \cdot mol\text{-}rxn}$$

$$\Delta_r G° = \Delta_r H° - T \Delta_r S° = 126.03 \; kJ - (298.15 \; K)(78.2 \frac{J}{K})(\frac{1.000 \; kJ}{1000 \; J}) = 103 \frac{kJ}{mol\text{-}rxn}$$

The reaction is not product-favored.

49. Calculate $\Delta_r G°$ for conversion to NO_2 from N_2O_4:

$$\Delta_r G° = - RT\ln K = - (8.3145 \times 10^{-3} \; kJ/K \cdot mol)(298 \; K) \ln 0.14 = 4.87 \; kJ$$

compare with the calculated $\Delta_f G°$ values:

$$\Delta_r G° = 2 \, \Delta_f G° \, [NO_2 \, (g)] - \Delta_f G° [N_2O_4 \, (g)] = (2 \cdot 51.23 \; kJ/mol) - (1 \cdot 97.73 \; kJ/mol) = 4.73 \; kJ$$

51. Calculate $\Delta_r G°$ for conversion of butane to isobutane, given K = 2.50:

$$\Delta_r G° = - RT\ln K = - (8.3145 \times 10^{-3} \text{ kJ/K}\bullet\text{mol})(298 \text{ K}) \ln 2.50 = -2.27 \frac{\text{kJ}}{\text{mol-rxn}}$$

53. For the reaction: $2 \text{ SO}_3 \text{ (g)} \rightarrow 2 \text{ SO}_2 \text{ (g)} + \text{O}_2 \text{ (g)}$

$\Delta_r H° = [2 \bullet \Delta_f H° \text{ SO}_2 \text{ (g)} + 1 \bullet \Delta_f H° \text{ O}_2 \text{ (g)}] - [2 \bullet \Delta_f H° \text{ SO}_3 \text{ (g)}]$

$$= [(2 \text{ mol})(- 296.84 \frac{\text{kJ}}{\text{mol}}) + 0] - [(2 \text{ mol})(-395.77 \frac{\text{kJ}}{\text{mol}})] = 197.86 \text{ kJ}$$

$\Delta_r S° = [2 \bullet S° \text{ SO}_2 \text{ (g)} + 1 \bullet S° \text{ O}_2 \text{ (g)}] - [2 \bullet S° \text{ SO}_3 \text{ (g)}]$

$$= [(2 \text{ mol})(248.21 \frac{\text{J}}{\text{K}\bullet\text{mol}}) + (1 \text{ mol})(205.07 \frac{\text{J}}{\text{K}\bullet\text{mol}})] - [(2 \text{ mol})(256.77 \frac{\text{J}}{\text{K}\bullet\text{mol}})]$$

$$= 187.95 \frac{\text{J}}{\text{K}\bullet \text{ mol-rxn}}$$

(a) Is the reaction product-favored at 25 °C ?:

$$\Delta_r G° = \Delta_r H° - T \Delta_r S° = 197.86 \text{ kJ} - (298.15 \text{ K})(187.95 \frac{\text{J}}{\text{K}})(\frac{1.000 \text{ kJ}}{1000 \text{ J}}) = 141.82 \frac{\text{kJ}}{\text{mol-rxn}}$$

The reaction is not product-favored.

(b) The reaction can become product-favored if there is some T at which $\Delta_r G° < 0$. To see if such a T is feasible, let's set $\Delta_r G° = 0$ and solve for T! *Remember that the units of energy must be the same, so let's convert units of J (for the entropy term) into units of kJ*

$\Delta_r G° = \Delta_r H° - T \Delta_r S°$

$$0 = 197.86 \text{ kJ} - T(0.18795 \frac{\text{kJ}}{\text{K}})$$

$$T = \frac{197.86 \text{ kJ}}{0.18795 \frac{\text{kJ}}{\text{K}}} = 1052.7 \text{ K} \quad \text{or} \quad (1052.7 - 273.1) = 779.6 \text{ °C}$$

(c) The equilibrium constant for the reaction at 1500 °C. Since we know that

$\Delta_r G° = \Delta_r H° - T\Delta_r S° = - RT\ln K$, we can solve for K if we know $\Delta_r G°$ at 1500 °C

$\Delta_r G° = \Delta_r H° - T \Delta_r S° = - RT \ln K$

$$= 197.86 \text{ kJ} - (1773 \text{ K})(187.95 \text{ J/K})(\frac{1.000 \text{ kJ}}{1000 \text{ J}}) = -135.4 \text{ kJ}$$

Substitute into the equation $(\Delta_r G° = - RT \ln K)$:

$$- 135.4 \text{ kJ} = - 8.314 \frac{\text{J}}{\text{K} \bullet \text{ mol}} \bullet \frac{1 \text{ kJ}}{1000 \text{ J}} \bullet 1773 \text{ K} \bullet \ln K$$

$$K = 9.7 \times 10^3 \quad \text{or} \quad 1 \times 10^4 \text{ (1 sf)}$$

55. Reaction: H_2S (g) + 2 O_2 (g) → H_2SO_4 (ℓ)
                $\Delta_fH°$(kJ/mol)   -20.63 0   - 814
                $S°$ (J/K • mol)   205.79   205.07   156.9
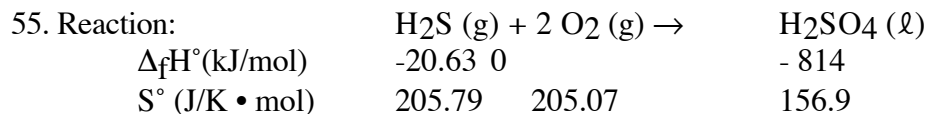
$\Delta_rH° = [(1 \text{ mol})(- 814 \dfrac{kJ}{mol})] - [(1 \text{ mol})(-20.63 \dfrac{kJ}{mol}) + 0] = -793 \dfrac{kJ}{mol\text{-rxn}}$

$\Delta_r S° = [(1 \text{ mol})(156.9 \dfrac{J}{K \bullet mol})] - [(1 \text{ mol})(205.79 \dfrac{J}{K \bullet mol}) + (2 \text{ mol})(205.07 \dfrac{J}{K \bullet mol})]$

$= -459.0 \dfrac{J}{K \bullet mol\text{-rxn}}$

$\Delta_r G° = \Delta_fH° - T \Delta_r S°$

$= - 793 \text{ kJ} - (298.15 \text{ K})(- 459.0 \dfrac{J}{K})(\dfrac{1.000 \text{ kJ}}{1000 \text{ J}}) = - 657 \dfrac{kJ}{mol\text{-rxn}}$

The reaction is product-favored at 25 °C ($\Delta G° < 0$) and enthalpy-driven ($\Delta_r H° < 0$)

57. Calculate the $\Delta_r G°$ for the transition of S_8 (rhombic) → S_8 (monoclinic)
    (a) At 80 °C $\Delta_r G° = \Delta_r H° - T \Delta_r S°$

$\Delta_r G° = 3.213 \text{ kJ} - (353 \text{ K})(0.0087 \dfrac{kJ}{K}) = 0.14 \dfrac{kJ}{mol\text{-rxn}}$

At 110 °C $\Delta_r G° = \Delta_r H° - T \Delta_r S°$

$\Delta_r G° = 3.213 \text{ kJ} - (383 \text{ K})(0.0087 \dfrac{kJ}{K}) = - 0.12 \dfrac{kJ}{mol\text{-rxn}}$

The rhombic form of sulfur is the more stable at lower temperature, while the monoclinic form is the more stable at higher temperature. The transition to monoclinic form is product-favored at temperatures above 110 degrees C.

    (b) The temperature at which $\Delta_r G° = 0$:

$\Delta_r G° = 3.213 \text{ kJ} - (T)(0.0087 \dfrac{kJ}{K})$ substituting: $0 = 3.213 \text{ kJ} - (T)(0.0087 \dfrac{kJ}{K})$

$T = \dfrac{3.213 \text{ kJ}}{0.0087 \frac{kJ}{K}} = 370 \text{ K} = 96 \text{ °C}$

IN THE LABORATORY

59. Is decomposition of silver(I) oxide product-favored at 25 °C ?

Calculate: $\Delta_r H°$ and $\Delta_r S°$:

$\Delta_r H° = ([4 \bullet \Delta_fH° \text{ Ag(s)}] + [1 \bullet \Delta_fH° \text{ O}_2\text{(g)}]) - [2 \bullet \Delta_fH° [\text{Ag}_2\text{O(s)}]$

$\Delta_r H° = 0 \text{ kJ} - [2 \text{ mol} \bullet -31.1 \text{ kJ/mol}] = 62.2 \dfrac{kJ}{mol\text{-rxn}}$

and for $\Delta_r S°$:

$\Delta_r S° = ([4 \cdot S° \text{ Ag(s)}] + [1 \cdot S° \text{ O}_2(g)]) - [2 \cdot S° \text{ [Ag}_2\text{O(s)]}$

$\Delta_r S° = ([4\text{mol} \cdot 42.55 \text{ J/K} \cdot \text{mol}] + [1\text{mol} \cdot 205.07 \text{ J/K} \cdot \text{mol}]) - [2\text{mol} \cdot 121.3 \text{ J/K} \cdot \text{mol}]$

$= [170.2 \text{ J/K} + 205.07 \text{ J/K}] - [242.6 \text{ J/K}] = +132.7 \text{ J/K}$

While enthalpic considerations do **not** favor product fomation, entropic considerations **do**. The Gibbs Free Energy change would be:

$\Delta_r G° = ([4 \cdot \Delta_f G° \text{ Ag(s)}] + [1 \cdot \Delta_f G° \text{ O}_2(g)]) - [2 \cdot \Delta_f G° \text{ [Ag}_2\text{O(s)]}$

$= (0 \text{ kJ}) - (2 \text{ mol} \cdot -11.32 \text{ kJ/mol}) = 22.64 \text{ kJ}$, so this change **does not favor** product formation.

The signs of $\Delta_r H°$ and $\Delta_r S°$ indicate that there **may be** some T at which the reaction is product-favored. So let's calculate the temperature at which $\Delta_r G° = 0$:

$\Delta_r G° = 62.2 \text{ kJ} - (T)(0.1327 \dfrac{\text{kJ}}{\text{K}})$ Note the conversion of ΔS units to kJ!
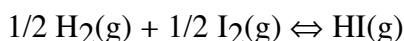
$0 = 62.2 \text{ kJ} - (T)(0.1327 \dfrac{\text{kJ}}{\text{K}})$

$T = \dfrac{62.2 \text{ kJ}}{0.1327 \dfrac{\text{kJ}}{\text{K}}} = 469 \text{ K} = 196°C$

At temperatures greater than 196 °C, the reaction would be product-favored.

61. Calculate $\Delta_f G°$ for HI(g) at 350 °C, given the following equilibrium partial pressures:

P(H$_2$)= 0.132 bar, P(I$_2$) = 0.295 bar, and P(HI) =1.61 bar. At 350 °C ,1 bar, I$_2$ is a gas.

$$1/2 \text{ H}_2(g) + 1/2 \text{ I}_2(g) \Leftrightarrow \text{HI(g)}$$

Calculate Kp: $\dfrac{P_{HI}}{P_{H_2}^{1/2} \cdot P_{I_2}^{1/2}} = \dfrac{1.61}{0.363 \cdot 0.543} = 8.16$

Knowing that $\Delta_r G° = -RT\ln K$, we can solve:

$\Delta_r G° = -RT\ln K = -(8.3145 \dfrac{J}{K \cdot mol})(623.15K)\ln 8.16 = -10,873J$ or -10.9 kJ/mol

63. (a) Calculate $\Delta_r G°$ and K for the reaction at 727 °C:

$\Delta_r G° = ([2 \cdot \Delta_f G° \text{ CO(g)}] + [1 \cdot \Delta_f G° \text{ TiC(s)}]) - ([1 \cdot \Delta_f G° \text{ [TiO}_2 \text{ (s)]} + [3 \cdot \Delta_f G° \text{ [C (s)]}])$

$\Delta_r G° = ([2\text{mol} \cdot -200.2 \text{ kJ/mol}] + [1 \text{ mol} \cdot -162.6 \text{ kJ/mol}]) - ([1 \text{ mol} \cdot -757.8 \text{ kJ/mol}] + [0])$

$= (-400.4 \text{ kJ} + -162.6 \text{ kJ}) - (-757.8 \text{ kJ}) = -563.0 \text{ kJ} + 757.8 \text{ kJ} = 194.8 \dfrac{\text{kJ}}{\text{mol-rxn}}$

K would equal:

$\Delta_r G° = -\,RT\ln K$ and $194.8 \text{ x } 10^3 \text{J} = -\,(8.3145 \dfrac{\text{J}}{\text{K} \bullet \text{mol}})(1000\text{K})\ln K$

[Note the conversion of the energy units of ΔG to accommodate J in the value of R!]

$\dfrac{194.8 \text{ x } 10^3 \text{J}}{-(8.3145 \dfrac{\text{J}}{\text{K} \bullet \text{mol}})(1000 \text{ K})} = \ln K = -23.43$ and $K = 6.68 \text{ x } 10^{-11}$

(b) The value of K indicates that the reaction is **not product-favored at this T**.

(c) Three of the four substances in the equilibrium are solids, hence do not appear in the K expression. The K expression would have the composition: $K = P^2(CO)$. According to LeChatelier's principle, reducing the concentration (and the pressure) of CO would tend to shift the equilibrium to the right, favoring product formation.

SUMMARY AND CONCEPTUAL QUESTIONS

65. An examination of the equation $Hg(\ell) \rightarrow Hg(g)$ shows that the equilibrium constant expression would be $Kp = P_{Hg(g)}$. So to find the temperature at which $Kp = 1.00$ bar and 1/760 bar, we need only to find the temperature at which the vapor pressure of mercury is 1.00 bar and 1/760 bar, respectively.

We can calculate the T for $Kp = 1.00$ bar easily. At the equilibrium point, we can calculate T at which $Kp = 1.00$bar if we know $\Delta G°$. Since at equilibrium, $\Delta G°= 0$, we can rewrite the equation: $\Delta G° = \Delta H° - T\Delta_r S°$ to read: $\Delta H°/\Delta_r S = T$

$\Delta_r H° = (1 \text{ mol})(61.38 \dfrac{\text{kJ}}{\text{mol}}) - (1 \text{ mol})(0) = 61.38 \text{ kJ}$ and for entropy:

$\Delta_r S° = (1 \text{ mol})(174.97 \dfrac{\text{J}}{\text{K} \bullet \text{mol}}) - (1 \text{ mol})(76.02 \dfrac{\text{J}}{\text{K} \bullet \text{mol}}) = 98.95 \dfrac{\text{J}}{\text{K}}$

Substituting into the equation:

$\Delta_r H°/\Delta_r S = T = (61.38 \text{ kJ} \bullet 1000 \text{ J/kJ})/ 98.95 \dfrac{\text{J}}{\text{K}} = 620.3 \text{ K}$. or 347.2 °C.

(b) Temperature at which $Kp = 1/760$ Using the Clausius-Clapeyron equation:

$\ln\left(\dfrac{P_2}{P_1}\right) = \dfrac{\Delta H}{R}\left(\dfrac{1}{T_1} - \dfrac{1}{T_2}\right)$ and $\ln\left(\dfrac{1}{760}\right) = \dfrac{61.38 \text{x} 10^3 \dfrac{\text{J}}{\text{mol}}}{8.3145 \dfrac{\text{J}}{\text{K} \bullet \text{mol}}}\left(\dfrac{1}{620.3\text{K}} - \dfrac{1}{T_2}\right)$

$$\frac{8.3145\dfrac{J}{K \bullet mol} \bullet -6.633}{61.38 \times 10^{3}\dfrac{J}{mol}} = \left(\frac{1}{620.3K} - \frac{1}{T_{2}}\right) \text{ so } -8.98 \times 10^{-4}\frac{1}{K} = \left(\frac{1}{620.3K} - \frac{1}{T_{2}}\right)$$

$- 1/T_2 = - 8.98 \times 10^{-4}$ 1/K $- 1.61 \times 10^{-3}$ $= -2.51 \times 10^{-3}$ and $T_2 = 398.3$ K or $125.2\,°C$.

So in summary, $Kp = 1$ at $347.2\,°C$ and is $1/760$ at $125.2\,°C$.

67. Following statements false or true?

(a) The entropy of a liquid increases on going from the liquid to the vapor state at any temperature. **True**. For a given substance, the entropy of the vapor state of that substance is greater than for the liquid state.

(b) An exothermic reaction will always be spontaneous. **False**. While exothermic reactions are *almost always spontaneous*, the entropy does play a role, and,should the entropy increase greatly enough, cause the reaction to be non-spontaneous (i.e. reactant-favored).

(c) Reactions with a + $\Delta_r H$ and a +Δ_r S can never be product-favored. **False**. At very high temperatures, such reactions can be product-favored (Δ_r G < 0).

(d) If Δ_rG is < 0, the reaction will have an equilibrium constant greater than 1. **True**. Since Δ_rG and K are related by the expression Δ_rG = -RT lnK, if ΔG < 0, then mathematically K will be greater than 1.

69. If we dissolve a solid (e.g. table salt), the process proceeds spontaneously ($\Delta_r G° < 0$).

If $\Delta_r H° = 0$, we can write: $\Delta_r G° = \Delta_r H° - T\Delta_r S°$ and $(-) = 0 - (+)\Delta_r S°$.

The only mathematical condition for which this equation is true is if $\Delta_r S° = +$, hence the process is entropy driven.

71. For the reaction: 2 C_2H_6(g) + 7 O_2(g) → 4 CO_2(g) + 6 H_2O(g)

(a) Predict whether signs of $\Delta_r S°$(system), $\Delta_r S°$(surroundings), Δ_r S°(universe) are greater than, equal to, or less than 0.

$\Delta_r S°$(system) will be > 0, since 9 mol of gas form 10 mol of gas as the reaction proceeds.

$\Delta_r S°$(surroundings) will be > 0, since the reaction liberates heat, and would increase the entropy of the surroundings. With both $\Delta_r S°$(system) and $\Delta_r S°$(surroundings) increasing, $\Delta_r S°$(universe) would also increase.

(b) Predict signs of $\Delta_r H°$, and $\Delta_r G°$: Since the reaction is exothermic, $\Delta_r H°$ would be "-". With a negative $\Delta_r H°$ and an increasing entropy, $\Delta_r G°$ would be "-" as well.

(c) Will value of Kp be very large, very small, or nearly 1? With the relatively large number of moles of carbon dioxide and water being formed, $\Delta_r H°$ will be *large and negative*, and with the increasing entropy $\Delta_r G°$ will also be relatively *large and negative*. Since $\Delta_r G$ = -RT lnK, we anticipate Kp being **very large**.

Will Kp be larger or smaller at temperatures greater than 298 K? Rearrange the expression $\dfrac{\Delta G}{RT} = -\ln K$. As T increases, the term on the left will decrease, resulting in a larger value of K (-lnK decreases-> so K increases).

73. Calculate the $\Delta_r S$ for (1) C(s) + 2 H$_2$ (g) $\rightarrow$ CH$_4$ (g)

$\Delta_r S_1° = (1 \text{ mol})(+186.26 \frac{J}{K•mol})$ -

$[(1 \text{mol})(+5.6 \frac{J}{K • mol}) + (2 \text{mol})(+130.7 \frac{J}{K • mol})] = -80.7 \frac{J}{K• mol\text{-rxn}}$

Calculate the $\Delta_r S$ for (2) CH$_4$(g) + $\frac{1}{2}$ O$_2$ (g) $\rightarrow$ CH$_3$OH(ℓ)

$\Delta_r S_2° = (1 \text{ mol})(+127.19 \frac{J}{K • mol})$ -

$[(1 \text{mol})(+186.26 \frac{J}{K • mol}) + (\frac{1}{2} \text{mol})(+205.07 \frac{J}{K • mol})] = -$

$161.60 \frac{J}{K• mol\text{-rxn}}$

Calculate the $\Delta_r S$ for (3) C(s) + 2 H$_2$ (g) + $\frac{1}{2}$ O$_2$ (g) $\rightarrow$ CH$_3$OH(ℓ)

$\Delta_r S_3° = (1 \text{ mol})(+127.19 \frac{J}{K •mol})$ -

$[(1 \text{mol})(+5.6 \frac{J}{K •mol}) + (2 \text{mol})(+130.7 \frac{J}{K •mol}) + (\frac{1}{2} \text{mol})(+205.07 \frac{J}{K •mol})]$

$= -242.3 \frac{J}{K• mol\text{-rxn}}$

So $\Delta_r S_1° + \Delta_r S_2° = (-80.7 \frac{J}{K}) + (-161.60 \frac{J}{K}) = -242.3 \frac{J}{K• mol\text{-rxn}}$

75. (a) Confirm that   Mg(s) + 2 H$_2$O(ℓ) $\rightarrow$ Mg(OH)$_2$ (s) + H$_2$(g) is a spontaneous reaction.

	Mg(s)	H$_2$O	Mg(OH)$_2$	H$_2$
$\Delta_f H°$ (kJ/mol)	0	-285.83	-924.54	0
S° (J/K • mol)	32.67	69.95	63.18	130.7

$\Delta_r H° = [(1 \text{ mol})(-924.54 \frac{kJ}{mol}) + (1 \text{mol})(0)] - [(1 \text{mol})0 + (2 \text{ mol})(-285.83 \frac{kJ}{mol})]$

$= -352.88 \frac{kJ}{mol\text{-rxn}}$

$$\Delta_r S° = [(1 \text{ mol})(63.18 \frac{J}{K \bullet mol}) + (1 \text{mol})(130.7 \frac{J}{K \bullet mol})] -$$

$$[(1 \text{mol})(32.67 \frac{J}{K \bullet mol}) + (2 \text{ mol})(69.95 \frac{J}{K \bullet mol})]$$

$$= 21.31 \frac{J}{K \bullet \text{mol-rxn}}$$

$\Delta_r G° = \Delta_f H° - T \Delta_r S°$

$$= -352.88 \text{ kJ} - (298.15 \text{ K})(21.31 \frac{J}{K})(\frac{1.000 \text{ kJ}}{1000 \text{ J}}) = -359.23 \frac{kJ}{\text{mol-rxn}}$$

With a negative $\Delta_r G°$, we anticipate the reaction to be spontaneous.
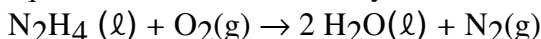
(b) Mass of Mg to produce sufficient energy to heat 225 mL of water (D = 0.996 g/mL) from 25°C to the boiling point (100 °C)? [100-25 = 75 °C or 75K]

Heat required: 225 mL • 0.996 g/mL • 4.184 J/g•K • 75 K. = 70,322.58 J or 70.3 kJ

The $\Delta_r H°$ =-352.88 kJ for 1 mol of Mg.

$$\frac{70.3 \text{kJ}}{1} \bullet \frac{1 \text{ mol Mg}}{352.88 \text{ kJ}} = 0.2 \text{ mol Mg or } 24.3 \text{ g/mol} \bullet 0.2 \text{ mol} = 4.84 \text{ g Mg}$$

77. (a) Equation for the reaction of hydrazine and oxygen.

$N_2H_4 (\ell) + O_2(g) \rightarrow 2 H_2O(\ell) + N_2(g)$

Oxygen is the **oxidizing agent,** and hydrazine is the **reducing agent.** There are several ways to assess this. Note that the oxidation state for O_2 is 0 (as reactant) and –2 (as product)—it has been reduced (by hydrazine). Note that hydrazine **loses H**—in going from reactant to product—a definition for being oxidized.

(b) Calculate $\Delta_r H°, \Delta_r S°$, and $\Delta_r G°$:

$\Delta_r H° = [2 \bullet \Delta_f H° \ H_2O (\ell) + 1 \bullet \Delta_f H° \ N_2 (g)] - [1 \bullet \Delta_f H° \ N_2H_4 (\ell) + 1 \bullet \Delta_f H° \ O_2 (g)]$

$$= [(2 \text{ mol})(-285.830 \frac{kJ}{mol}) + 0] - [(1 \text{ mol})(50.63 \frac{kJ}{mol}) + 0] = -622.29 \frac{kJ}{\text{mol-rxn}}$$

$\Delta_r S° = [2 \bullet S° H_2O (\ell) + 1 \bullet S° \ N_2 (g)] - [1 \bullet S° \ N_2H_4 (\ell) + 1 \bullet S° \ O_2 (g)]$

$$= [(2 \text{ mol})(69.95 \frac{J}{K\bullet mol}) + (1 \text{ mol})(191.56 \frac{J}{K\bullet mol})] -$$

$$[(1 \text{ mol})(121.52 \frac{J}{K\bullet mol}) + (1 \text{ mol})(205.07 \frac{J}{K\bullet mol})] = 4.87 \frac{J}{K \bullet \text{mol-rxn}}$$

$\Delta_r G° = \Delta_r H° - T \Delta_r S°$

$$= -622.29 \text{ kJ} - (298 \text{ K})(4.87 \frac{J}{K})(\frac{1.000 \text{ kJ}}{1000. \text{ J}}) = -623.74 \frac{kJ}{\text{mol-rxn}}$$

(c) T change of 5.5×10^4 L of water (assuming 1 mole of N_2H_4 reacts:

　　1 mol of hydrazine releases -622.29 kJ,

　　Heat $= m \cdot c \cdot \Delta t$ 　[Assume D of water $= 0.996$ g/mL]

　　622.29×10^3 J $= 5.5 \times 10^4$ L $\cdot$ 996 g/L $\cdot$ 4.184 J/g $\cdot$K $\cdot \Delta t$.

$$\frac{6.2229 \times 10^5 \, J}{\left(5.5 \times 10^4 \, L \cdot 996 \, \frac{g}{L} \cdot 4.184 \, \frac{J}{g \cdot K}\right)} = \Delta t. \text{ Solving for } \Delta t \text{ gives: } 2.7 \times 10^{-3} \text{ K.}$$

(d) Solubility of $O_2 = 0.000434$ g O_2/100g water.

　　5.5×10^4 L $\cdot$ 996 g/L $\cdot$ 4.34×10^{-4} g O_2/100g water $\cdot$ 1 mol O_2/32.00 g O_2

　　7.5 mol O_2 (or approximately 240 g)

(e) If hydrazine is present in 5% solution, what mass of hydrazine solution is needed to consume the O_2 present?

$$\frac{7.4 \text{ mol } O_2}{1} \cdot \frac{1 \text{ mol } N_2H_4}{1 \text{ mol } O_2} \cdot \frac{32.05 \text{ g } N_2H_4}{1 \text{ mol } N_2H_4} \cdot \frac{100 \text{ g solution}}{5.00 \text{ g } N_2H_4} = 4.8 \times 10^3 \text{ g solution}$$

　　　　　　　　　　　　　　　　　　　　　　　　　　　　(2 sf)

(f) Assuming N_2 escapes as gas, calculate V of N_2 at STP,

　　The balanced equation tells us that 7.4 mol of O_2 will liberate 7.4 mol of N_2. At STP, 7.4 mol of this gas will occupy (7.4 mol $\cdot$ 22.4 L/mol) or 170 L (2 sf)

79. The key phrase needed to answer the question: "What is the sign......" is "Iodine dissolves readily...." . This phrase tell us that $\Delta_r G°$ is negative.

Enthalpy-driven processes are exothermic. The "neutrality" of the ΔH for this reaction tells us that the process is NOT enthalpy-driven. Since the iodine goes from the solid state to the "solution" state, we anticipate an increase in entropy, and would therefore state that the process is entropy-driven.

81. (a) According to Screen 19.6 of ChemistryNow, the spontaneity decreases as T increases.
　　(b) There is no T between 400K and 1000K at which the reaction is spontaneous.

83. (a)Calculate $\Delta_r G°$ at 298K, 800 K, and 1300 K for the reaction:$N_2(g) + 3 \, H_2(g) \Leftrightarrow 2 \, NH_3(g)$

　　At 298K: $\Delta_r H° = $ (2 mol $\cdot$-45.90 kJ/mol)- (0 + 0) = -91.80 kJ

　　and $\Delta_r S° = $ (2 mol $\cdot$ 192.77 J/K$\cdot$mol) - (1mol $\cdot$191.56 J/K$\cdot$mol + 3mol $\cdot$ 130.7 J/K$\cdot$mol)
　　= -198.12 J/K 　and

$$\Delta_r G° = \Delta_f H° - T\Delta_r S° = -91.80 \text{ kJ} – (298 \text{ K})(-0.19812 \text{ kJ/K}) = -32.74 \frac{\text{kJ}}{\text{mol-rxn}}$$

At 800K:

$$\Delta_r G° = \Delta_f H° - T\Delta_r S° = -107.4 \text{ kJ} – (800\text{K})(-0.2254 \text{ kJ//K}) = 72.92 \frac{\text{kJ}}{\text{mol-rxn}}$$

At 1300 K:

$$\Delta_r G° = \Delta_f H° - T\Delta_r S° = - 112.4 \text{ kJ} – (1300\text{K})(-0.2280 \text{ kJ/K}) = 184.0 \frac{\text{kJ}}{\text{mol-rxn}}$$

A quick examination of the values of $\Delta_r G°$ indicates that the free energy change becomes more positive as T increases.

(b) Calculate K for the reaction at 298K, 800K, 1300K:

At 298K:

$$\frac{- 32.74 \text{ x } 10^3 \text{J}}{-(8.3145 \frac{\text{J}}{\text{K•mol}})(298 \text{ K})} = \ln K = 13.21 \text{ and K } = 5.48 \text{ x } 10^5$$

At 800K:

$$\frac{72.92 \text{ x } 10^3 \text{J}}{-(8.3145 \frac{\text{J}}{\text{K•mol}})(800 \text{ K})} = \ln K = -10.96 \text{ and K} = 1.73 \text{ x } 10^{-5}$$

At 1300 K:

$$\frac{184 \text{ x } 10^3 \text{J}}{-(8.3145 \frac{\text{J}}{\text{K•mol}})(1300 \text{ K})} = \ln K = -17.02 \text{ and K} = 4.05 \text{ x } 10^{-8}$$

(c) For which T will mole fraction of NH_3 be largest

The "bottom line" is easy to assess. The partial pressure of ammonia will be greatest for the temperature for which K is greatest (298 in this case).