Chapter 7 Homework Solutions

7.1   (1/2) N_2(g) + (3/2) H_2(g) $\rightarrow$ NH_3(g) $\Delta_r G^o$ = -16.5 kJ
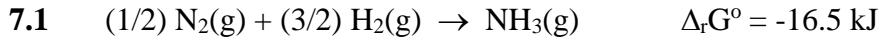
P_{NH3} = 4.0 bar P_{N2} = 3.0 bar P_{H2} = 1.0 bar   T = 298 K

$$\Delta_r G = \Delta_r G^o + nRT \ln Q = \Delta_r G^o + nRT \ln\left(\frac{P_{NH_3}}{P_{N_2}^{1/2} \cdot P_{H_2}^{3/2}}\right)$$

$$= -16.5\,kJ + (1\,mol)(8.314\,J/mol \cdot K)(298\,K)\ln\left(\frac{4\,bar}{(3\,bar)^{1/2}(1\,bar)^{3/2}}\right)$$

$$= -16.5\,kJ + 2070\,J = -16.5\,kJ + 2.1\,kJ = -14.4\,kJ$$

Because $\Delta_r G < 0$, under these conditionsm, the reaction is spontaneous towards products.

7.2   A + B = 2 C $K_1 = \dfrac{[C]^2}{[A][B]} = 3.4x10^4$

(a) 2 A + 2 B = 4 C $K_2 = \dfrac{[C]^4}{[A]^2[B]^2} = K_1^2 = (3.4x10^4)^2 = 1.2x10^9$

(b) (1/2) A + (1/2) B = C $K_3 = \dfrac{[C]}{[A]^{1/2}[B]^{1/2}} = \sqrt{K_1} = \sqrt{3.4x10^4} = 1.8x10^2$

7.3 ΔG^o = -RTlnK
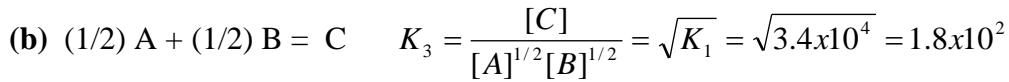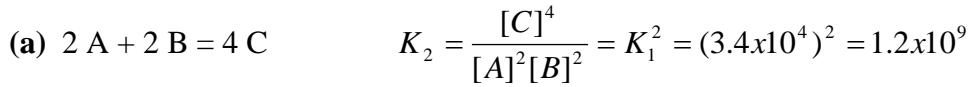
$$\ln K = -\frac{\Delta G^o}{RT} = -\frac{-3.67x10^3\,J/mol}{(8.314\,J/mol \cdot K)(400\,K)} = 1.10$$

$$K = e^{+1.10} = 3.01$$

7.4 ΔH^o = +224 kJ/mol (indep. of T) ΔG^o = +33 kJ/mol at 1280 K
We'll use data at 1280 K to determine ΔS^o.
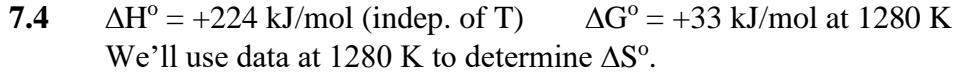
$$\Delta G^o = \Delta H^o - T\Delta S^o \rightarrow \Delta S^o = \frac{\Delta H^o - \Delta G^o}{T} = \frac{224\,kJ/mol - 33\,kJ/mol}{1280\,K} = 0.149\,kJ/mol \cdot K$$

K = 1 corresponds to ΔG^o = 0. Larger K's correspond to negative ΔG^o's. We'll find temperature where ΔG^o = 0

$$0 = \Delta H^o - T\Delta S^o \rightarrow T = \frac{\Delta H^o}{\Delta S^o} = \frac{224\,kJ/mol}{0.149\,kJ/mol \cdot K} = 1503\,K - 273 = 1230\,^oC$$

7.5   Calculate $\Delta_r S^\circ$ and $\Delta_r H^\circ$ from data in the table and then calculate: $\Delta_r G^\circ = \Delta_r H^\circ - T\Delta_r S^\circ$

Compound	$\Delta_f H^\circ$	S_m°
Al_2O_3	-1675.7 kJ/mol	50.9 J/mol-K
Si		18.8
SiO_2	-910.941.8	
Al		28.3

$$\Delta H^\circ = 3\Delta_f H^\circ(SiO_2) + 4\Delta_f H^\circ(Al) - [2\Delta_f H^\circ(Al_2O_3) + 3\Delta_f H^\circ(Si)]$$
$$= 3(-910.9) + 4(0) - [2(-1675.7) + 3(0)] = +618.7\,kJ$$

$$\Delta S^\circ = 3S_m^o(SiO_2) + 4S_m^o(Al) - [2S_m^o(Al_2O_3) + 3S_m^o(Si)]$$
$$= 3(41.8) + 4(28.3) - [2(50.9) + 3(18.8)] = +80.4\,J/K = +0.0804\,kJ/K$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = +618.7\,kJ - (298\,K)(0.0804\,kJ/K$$
$$= +594.7\,kJ = 595\,kJ$$

7.6   Pyruvate⁻ + NADH + H⁺ → Lactate⁻ + NAD⁺

$\Delta G^{o'} = \Delta G^o + x(40\ kJ/mol) = -66.6\ kJ/mol + 1 \times 40\ kJ/mol = -26.6\ kJ/mol$

7.7 $SbCl_5(g) = SbCl_3(g) + Cl_2(g)$

$K = 3.5x10^{-4}$ $P_{SbCl5} = 0.15$ bar $P_{SbCl3} = 0.20$ bar $P_{Cl2} = ??$

$$K = \frac{P_{SbCl_3} \cdot P_{Cl_2}}{P_{SbCl_5}} \quad \rightarrow \quad P_{Cl_2} = K\frac{P_{SbCl_5}}{P_{SbCl_3}} = 3.5x10^{-4}\frac{0.15\,bar}{0.20\,bar} = 2.6x10^{-4}\,bar$$

7.8

	$N_2(g)$	+	$3H_2(g)$	É	$2NH_3(g)$
Initial/atm	0.020		0.020		0
Change	$-x$		$-3x$		$+2x$
Equil.	$0.020 - x$		$0.020 - 3x$		$2x$

$$K = 0.036 = \frac{P_{NH_3}^2}{P_{N_2}P_{H_2}^3} = \frac{(2x)^2}{(0.02 - x)(0.02 - 3x)^3} \approx \frac{(2x)^2}{(0.02)(0.02)^3} = 2.5x10^7\,x^2$$

We have assumed that x << 0.02 and 3x << 0.02 because K << 1

$$x^2 = \frac{0.036}{2.5x10^7} = 1.44x10^{-9} \rightarrow x = 3.8x10^{-5}$$

\\Note that x and 3x are indeed << 0.02. This would not be correct at temperatures where

$K \geq \sim 1$.

$P_{N2} \approx 0.02$ bar

$P_{H2} \approx 0.02$ bar

$P_{NH3} = 2x = 2 \times 3.8\times10^{-5} = 7.6\times10^{-5}$ bar

7.9 $K_1 = 337$ $T_1 = 100\ ^\circ C = 373$ K $K_2 = 7.1\times10^{-5}$ $T_2 = 500\ ^\circ C = 773$ K

(a) $\ln\left(\dfrac{K_2}{K_1}\right) = -\dfrac{\Delta H^o}{R}\left[\dfrac{1}{T_2} - \dfrac{1}{T_1}\right]$

Therefore,

$$\Delta H^o = -\frac{R\ln(K_2/K_1)}{\dfrac{1}{T_2}-\dfrac{1}{T_1}} = -\frac{(8.314\,J/mol\cdot K)\ln(7.1x10^{-5}/337)}{\dfrac{1}{773}-\dfrac{1}{373}} = -92{,}130\,J/mol = -92.1kJ/mol$$

At T_1, $\Delta S^o/R = \ln(K_1) + \Delta H^o/RT1 = \ln(337) + (-92{,}130)/(8.31*373) = -23.9$

$\Delta S^o = -23.9(8.31) = -199$ J/mol-K $= -200$ J/mol-K

(b) $K_3 = ??$ at $T_3 = 300\ ^\circ C = 573$ K

$$\ln(K_3/K_1) = -\frac{\Delta H^o}{R}\left[\frac{1}{T_3}-\frac{1}{T_1}\right] = -\frac{-92130\,J/mol}{8.314\,J/mol\cdot K}\left[\frac{1}{573\,K}-\frac{1}{373}\right] = -10.37$$

$K_3 = K_1 e^{-10.37} = (337)(3.14x10^{-5}) = 0.011$

(c) $P_{N2} = 1.0 - x$ $P_{H2} = 3.0 - 3x$ $P_{NH3} = 2x$

$$K = 7.1x10^{-5} = \frac{P_{NH_3}^2}{P_{N_2}P_{H_2}^3} = \frac{(2x)^2}{(1.0-x)(3.0-3x)^3} \approx \frac{4x^2}{(1.0)(3.0)^3} = \frac{4}{27}x^2$$

$x^2 = 4.79x10^{-4}$ $\rightarrow$ $x = 0.022$ bar

$P_{NH3} = 2x = 0.044$ bar

$P_{N2} = 1.0 - x = 0.98$ bar

$P_{H2} = 3.0 - 3x = 2.93$ bar

(d) ΔG^o = -RTln(K) = -(8.314 J/mol-K)(773 K)ln(7.1×10^{-5}) = +61,400 J/mol

$$\Delta G = \Delta G^o + RT \ln\left(\frac{P_{NH_3}^2}{P_{N_2} P_{H_2}^3}\right)$$

$$= 61,400 \, J / mol + (8.314 \, J / mol \cdot K)(773 K) \ln\left(\frac{(2.5)^2}{(0.2)(0.2)^2}\right)$$

$$= 61,400 \, J / mol + 53,200 \, J / mol = 114,600 \, J / mol = 115 \, kJ / mol$$

7.10 FDP = GAP + DHAP   K = 8.9×10^{-5} at T = 25 °C = 298 K

    (a) [FDP] = 0.10 - x   [GAP] = x   [DHAP] = x

$$K = \frac{[GAP][DHAP:]}{[FDP:]} = \frac{x \cdot x}{0.1 - x} = 8.9 x 10^{-5}$$

$x^2 + 8.9\times10^{-5}x - 8.9\times10^{-6} = 0 = ax^2 + bx + c$

$$x = \frac{-b + \sqrt{b^2 - 4ac}}{2a} = \frac{-8.9 x 10^{-5} + \sqrt{(8.9 x 10^{-5})^2 - 4(1)(-8.9 x 10^{-6})}}{2} = 2.94 x 10^{-3}$$

[FDP] = 0.10 - x = 0.997 M

[GAP] = [DHAP] = x = 2.94×10^{-3} M

Note: Approximate solution by setting 0.1-x $\approx$ 0.1 in denominator of eqn. gives x = 2.98×10^{-3} M

    (b) [FDP] = 1×10^{-5} - x   [GAP[= x   [DHAP] = x

$$K = \frac{[GAP][DHAP:]}{[FDP:]} = \frac{x \cdot x}{1 x 10^{-5} - x} = 8.9 x 10^{-5}$$

Solve using quadratic formula to get: x = 9.1×10^{-6} M

[FDP] = 1×10^{-5} - 9.1×10^{-6} = 9×10^{-7} M

[GAP] = [DHAP] = x = 9.1×10^{-6} M

Note: Approx. solution by setting 1×10^{-5} - x $\approx$ 1×10^{-5} in denominator of eqn. gives x = 3.0×10^{-5} M

This is twice the initial concentration of [FDP]; i.e. Approximation that x << c_o is not valid

    (c) ΔG^o = -RTln(K) = -8.314 J/mol-K(298 K)ln(8.9×10^{-5}) = +23,100 J/mol

$$\Delta G = \Delta G^o + RT \ln\left(\frac{[GAP][DHAP]}{[FDP]}\right)$$

$$= 23,100 \, J / mol + (8.314 \, J / mol \cdot K)(298 K) \ln\left(\frac{(2 x 10^{-5})(2 x 10^{-5})}{0.5}\right)$$

$$= 23,100 \, J / mol + (-51,900 \, J / mol) = -28,800 \, J / mol = -28.8 \, kJ / mol$$

7.11 $\Delta G^o = \Delta H^o - T\Delta S^o = -RT\ln(K)$

$$\ln(K) = \frac{\Delta H^o - T\Delta S^o}{-RT} = -\frac{\Delta H^o}{R}\frac{1}{T} + \frac{\Delta S^o}{R} = Slope \cdot \frac{1}{T} + Int$$

Slope = $-\Delta H^o/R$ Int = $\Delta S^o/R$

Two points on Graph: (1) $\ln(K_1) = 3.0$ at $1/T_1 = 0.004$ K^{-1}

(2) $\ln(K_2) = 6.0$ at $1/T_2 = 0.00475$ K^{-1}

$$Slope = \frac{6.0 - 3.0}{0.00475\,K^{-1} - 0.004\,K^{-1}} = 4000\,K = -\Delta H^o / R$$

$\Delta H^o = -R \times 4000\ K = -(8.314\ \text{J/mol-K})(4000\ K) = -3.33\text{x}10^4$ J/mol = -33.3 kJ/mol

$$Int = \ln(K_1) - Slope\frac{1}{T_1} = 3.0 - (4000\,K)(0.004) = -13.0 = \Delta S^o / R$$

$\Delta S^o = -13.0(R) = -13.0(8.314\ \text{J/mol-K}) = -108$ J/mol-K

7.12 (1) For $[L]_1 = [L]_{out} = 0.110$ M , $[L]_{bound} = [L]_{in} - [L]_{out} = 0.211 - 0.110 = 0.101$ M

$R_1 = [L]_{bound} / [P]_{tot} = 0.101$ M / 0.004 M = 25.3

(2) For $[L]_2 = [L]_{out} = 0.620$M , $[L]_{bound} = [L]_{in} - [L]_{out} = 0.785 - 0.620 = 0.165$ M

$R_2 = [L]_{bound} / [P]_{tot} = 0.165$ M / 0.004 M = 41.3

$$R = \frac{n[L]}{K + [L]} \quad \rightarrow \quad \frac{1}{R} = \frac{K + [L]}{n[L]} = \frac{K}{n}\frac{1}{[L]} + \frac{1}{n} = Slope\frac{1}{[L]} + Int$$

Slope = K/n   Int = 1/n

$$Slope = \frac{\dfrac{1}{R_2} - \dfrac{1}{R_1}}{\dfrac{1}{[L]_2} - \dfrac{1}{[L]_1}} = \frac{\dfrac{1}{41.3} - \dfrac{1}{25.3}}{\dfrac{1}{0.620M} - \dfrac{1}{0.110M}} = 2.05x10^{-3}\,M$$

$$Int = \frac{1}{R_1} - Slope\frac{1}{[L]_1} = \frac{1}{25.3} - (2.05x10^{-3}\,M)\frac{1}{0.101M} = 2.09x10^{-2}$$

n = 1/Int = 1/2.09x10^{-2} = 48

Slope = K/n $\rightarrow$ K = n x Slope = 48 x 2.05x10^{-3} = 0.098

7.13 Two points on Graph: (1) $1/R_1 = 0.04$ at $1/[L]_1 = 2.0$ M^{-1}

(2) $1/R_2 = 0.06$ at $1/[L]_2 = 5.0$ M^{-1}

$$Slope = \frac{\dfrac{1}{R_2} - \dfrac{1}{R_1}}{\dfrac{1}{[L]_2} - \dfrac{1}{[L]_1}} = \frac{0.06 - 0.04}{5.0\,M^{-1} - 2.0\,M^{-1}} = 6.67x10^{-3}\,M$$

$$Int = \frac{1}{R_1} - Slope\frac{1}{[L]_1} = 0.04 - (6.67x10^{-3}\,M)(2.0\,M^{-1}) = 2.67x10^{-2}$$

$$\frac{1}{R} = \frac{K + [L]}{n[L]} = \frac{K}{n}\frac{1}{[L]} + \frac{1}{n} = Slope\frac{1}{[L]} + Int$$

n = 1/Int = $1/2.67x10^{-2}$ = 37.5 ≈ 38

Slope = K/n → K = n x Slope = 37.5 x $6.67x10^{-3}$ = 0.250

7.14 Glucose + 2NAD$^+$ + 2ADP + P$_i^-$ → 2 CH$_3$COCO$_2^-$ + 2NADH + 2ATP + 2H$^+$

$\Delta G^{o'} = \Delta G^o$ -x(40 kJ/mol)

$\Delta G^o = \Delta G^{o'}$ + x(40 kJ/mol) = -80.7 kJ + (2 mol)(40 kJ/mol) = -0.7 kJ/mol