Solutions 9

1. (a) $\Delta_r G^{\varnothing} = -RT \ln K = -(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (400 \text{ K}) \times \ln 2.07 = -2419.54 \text{ J mol}^{-1} =$ **-2.42 kJ mol^{-1}**

(b) $K = \exp(-\Delta_r G^{\varnothing}/RT) = \exp\{-3670 \text{ J mol}^{-1}/[(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (400 \text{ K})]\} =$ **3.01**

2. $2\ H_2O(g) \leftrightarrows 2\ H_2(g) + O_2(g)$

Write equilibrium table:

	H_2O	H_2	O_2
Initial	n	0	0
Change to reach equilibrium	$-\alpha n$	$+\alpha n$	$+(1/2)\alpha n$
Amount at equilibrium	$(1 - \alpha)n$	αn	$(1/2)\alpha n$
Mole fraction	$\dfrac{1-\alpha}{1+\frac{1}{2}\alpha}$	$\dfrac{\alpha}{1+\frac{1}{2}\alpha}$	$\dfrac{\frac{1}{2}\alpha}{1+\frac{1}{2}\alpha}$
Partial pressure	$\dfrac{1-\alpha}{1+\frac{1}{2}\alpha}p$	$\dfrac{\alpha}{1+\frac{1}{2}\alpha}p$	$\dfrac{\frac{1}{2}\alpha}{1+\frac{1}{2}\alpha}p$

Here we use p in the sense of $p/p^{\varnothing}$.

$$K = \frac{\left(\dfrac{\alpha p}{1+1/2\,\alpha}\right)^2\left(\dfrac{1/2\,\alpha p}{1+1/2\,\alpha}\right)}{\left(\dfrac{(1-\alpha)p}{1+1/2\,\alpha}\right)^2} = \frac{\alpha^3 p}{2(1-\alpha)^2(1+1/2\,\alpha)}$$

(a) $K = (0.0177)^3/\{2(1 - 0.0177)^2(1 + 0.0177/2) =$ **2.848×10^{-6}**

(b) $\Delta_r G^{\varnothing} = -RT \ln K = -(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (400 \text{ K}) \times \ln 2.848\times10^{-6} =$ **240 kJ mol^{-1}**

(c) **$\Delta_r G = 0$** – because the reaction is at equilibrium

3. $N_2O_4(g) \leftrightarrows 2\ NO_2(g)$

Write equilibrium table:

	N_2O_4	NO_2
Initial	n	0
Change to reach equilibrium	$-\alpha n$	$+2\alpha n$
Amount at equilibrium	$(1 - \alpha)n$	$2\alpha n$
Mole fraction	$\frac{1-\alpha}{1+\alpha}$	$\frac{2\alpha}{1+\alpha}$
Partial pressure	$\frac{1-\alpha}{1+\alpha}p$	$\frac{2\alpha}{1+\alpha}p$

(a) $K = \left(\frac{2\alpha p}{1+\alpha}\right)^2 \Big/ \left(\frac{1-\alpha}{1+\alpha}p\right) = \frac{4\alpha^2 p}{1-\alpha^2}$ = $4(0.1846)^2/(1-0.1846^2)$ = **0.1411**

(b) $\Delta_r G^\ominus = -RT \ln K$ = -(8.314 J K^{-1} mol^{-1})×(400 K)×ln 0.1411 = **4.855 kJ mol^{-1}**

(c) ln K(373.15 K) = ln K(298.15 K) – ($\Delta_r H^\ominus/R$)×{1/(373.15 K) – 1/(298.15 K)}

K(373.15 K) = **14.556**

4. (a) $\Delta_r G^\ominus = \Delta_f G^\ominus(Pb,s) + \Delta_f G^\ominus(CO_2,g) - \Delta_f G^\ominus(PbO,s) - \Delta_f G^\ominus(CO,g)$ = (-394.36 kJ mol^{-1}) – (-188.93 kJ mol^{-1}) – (-137.17 kJ mol^{-1}) = **-68.26 kJ mol^{-1}**

$K = \exp(-\Delta_r G^\ominus/RT)$ = exp{-68260 J mol^{-1}/[(8.314 J K^{-1} mol^{-1})×(298 K)]} = **9.22×10^{11}**

(b) $\Delta_r H^\ominus = \Delta_f H^\ominus(Pb,s) + \Delta_f H^\ominus(CO_2,g) - \Delta_f H^\ominus(PbO,s) - \Delta_f H^\ominus(CO,g)$ = (-393.51 kJ mol^{-1}) – (-218.99 kJ mol^{-1}) – (-110.53 kJ mol^{-1}) = -63.99 kJ mol^{-1}

ln K(400 K) = ln K(298 K) – ($\Delta_r H^\ominus/R$)×{1/(400 K) – 1/(298 K)}

K(400 K) = **1.27×10^9**

$\Delta_r G^\ominus$(400 K) = $-RT$ ln K(400 K) = -(8.314 J K^{-1} mol^{-1})×(400 K)×ln1.272×10^9 = **-69.72 kJ mol^{-1}**

5. $$K = \frac{a_{CO}a_{H_2}}{a_{H_2CO}} \approx \frac{p_{CO}p_{H_2}}{p_{H_2CO}} = \frac{x_{CO}p\,x_{H_2}p}{x_{H_2CO}p} = \frac{x_{CO}x_{H_2}}{x_{H_2CO}}p = K_x p$$

In order to keep K constant when the total pressure increases by a factor of 2 K_x should be decreased by a factor of 2 or by **50%**.

6. $H_2(g) + I_2(g) \leftrightarrows 2\,HI(g)$

	H_2	I_2	HI
Initial	0.3	0.4	0.2
Change to reach equilibrium	$-x$	$-x$	$+2x$
Amount at equilibrium	$0.3 - x$	$0.4 - x$	$0.2 + 2x$

Mole fraction	$(0.3 - x)/0.9$	$(0.4 - x)/0.9$	$(0.2 + 2x)/0.9$

Pressure cancels out in the expression for K here because the number of gas molecules does not change in this reaction.

$$K = \frac{\left(\left(0.2 + 0.2x\right)/0.9\right)^2}{\left(\left(0.3 - x\right)/0.9\right)\left(\left(0.4 - x\right)/0.9\right)} = \frac{\left(0.2 + 0.2x\right)^2}{\left(0.3 - x\right)\left(0.4 - x\right)} = 870$$

This equation reduces to the following quadratic equation:

$866\,x^2 + 609.5\,x + 104.36\,x = 0$

Use the quadratic formula to solve this equation:

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \qquad x = 0.2933 \qquad \text{and} \qquad x = 0.4108$$

We chose $x = 0.2933$ because x should be smaller than 0.3 (the reaction cannot consume more than the initial amount of H_2, which is 0.3 mol).

Thus, $x = 0.2933$ and the amounts of each species at equilibrium are:

H_2: 0.3 – 0.2933 = **0.0067**; I_2: 0.4 – 0.2933 = **0.1067**; HI: 0.2 + 2×0.2933 = **0.7866** (all in mol)

7. $A + 3\,B \leftrightarrows 2\,C$

	A	B	C
Initial	n	$3n$	0
Change to reach equilibrium	$-\xi n$	$-3\xi n$	$+2\xi$
Amount at equilibrium	$(1 - \xi)n$	$3(1 - \xi)n$	2ξ
Mole fraction	$\frac{1-\xi}{2(2-\xi)}$	$\frac{3(1-\xi)}{2(2-\xi)}$	$\frac{\xi}{2-\xi}$
Partial pressure	$\frac{1-\xi}{2(2-\xi)}p$	$\frac{3(1-\xi)}{2(2-\xi)}p$	$\frac{\xi}{2-\xi}p$

$$K = \frac{\left(p_C/p^{\Theta}\right)^2}{\left(p_A/p^{\Theta}\right)\left(p_B/p^{\Theta}\right)^3} = \frac{\left(\dfrac{\xi}{2-\xi}\right)^2}{\left(\dfrac{1-\xi}{2(2-\xi)}\right)\left(\dfrac{3(1-\xi)}{2(2-\xi)}\right)^3} = \frac{16(2-\xi)^2\xi^2}{27(1-\xi)^4}\left(\frac{p^{\Theta}}{p}\right)^2$$

Introduce $a^2 = \frac{27}{16}K$ $$\frac{(2-\xi)^2\xi^2}{(1-\xi)^4} = a^2\left(\frac{p}{p^\Theta}\right)^2$$

$$(2-\xi)\xi = \left(ap/p^\Theta\right)(1-\xi)^2$$

$$\left(1-\frac{ap}{p^\Theta}\right)\xi^2 - 2\left(1-\frac{ap}{p^\Theta}\right)\xi + \frac{ap}{p^\Theta} = 0$$

Solving this quadratic equation gives $$\xi = 1-\left(\frac{1}{1+ap/p^\Theta}\right)^{1/2}$$