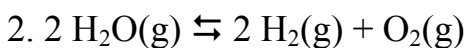


Solutions 9

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

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



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	$(1/2)\alpha n$
	$\frac{1 - \alpha}{1 + \frac{1}{2}\alpha}$	$\frac{\alpha}{1 + \frac{1}{2}\alpha}$	$\frac{\frac{1}{2}\alpha}{1 + \frac{1}{2}\alpha}$
Mole fraction			
	$\frac{1 - \alpha}{1 + \frac{1}{2}\alpha} p$	$\frac{\alpha}{1 + \frac{1}{2}\alpha} p$	$\frac{\frac{1}{2}\alpha}{1 + \frac{1}{2}\alpha} p$
Partial pressure			

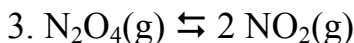
Here we use p in the sense of p/p° .

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

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

(b) $\Delta_r G^\circ = -RT \ln K = -(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (400 \text{ K}) \times \ln 2.848 \times 10^{-6} = \mathbf{240 \text{ kJ mol}^{-1}}$

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



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	$\frac{1 - \alpha}{1 + \alpha} p$	$\frac{2\alpha}{1 + \alpha} p$

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

$$(b) \quad \Delta_r G^\circ = -RT \ln K = -(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (400 \text{ K}) \times \ln 0.1411 = \mathbf{4.855 \text{ kJ mol}^{-1}}$$

$$(c) \quad \ln K(373.15 \text{ K}) = \ln K(298.15 \text{ K}) - (\Delta_r H^\circ / R) \times \{1/(373.15 \text{ K}) - 1/(298.15 \text{ K})\}$$

$$K(373.15 \text{ K}) = \mathbf{14.556}$$

$$4. (a) \quad \Delta_r G^\circ = \Delta_f G^\circ(\text{Pb}, s) + \Delta_f G^\circ(\text{CO}_2, g) - \Delta_f G^\circ(\text{PbO}, s) - \Delta_f G^\circ(\text{CO}, g) = (-394.36 \text{ kJ mol}^{-1}) - (-188.93 \text{ kJ mol}^{-1}) - (-137.17 \text{ kJ mol}^{-1}) = \mathbf{-68.26 \text{ kJ mol}^{-1}}$$

$$K = \exp(-\Delta_r G^\circ / RT) = \exp\{-68260 \text{ J mol}^{-1} / [(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K})]\} = \mathbf{9.22 \times 10^{11}}$$

$$(b) \quad \Delta_r H^\circ = \Delta_f H^\circ(\text{Pb}, s) + \Delta_f H^\circ(\text{CO}_2, g) - \Delta_f H^\circ(\text{PbO}, s) - \Delta_f H^\circ(\text{CO}, g) = (-393.51 \text{ kJ mol}^{-1}) - (-218.99 \text{ kJ mol}^{-1}) - (-110.53 \text{ kJ mol}^{-1}) = -63.99 \text{ kJ mol}^{-1}$$

$$\ln K(400 \text{ K}) = \ln K(298 \text{ K}) - (\Delta_r H^\circ / R) \times \{1/(400 \text{ K}) - 1/(298 \text{ K})\}$$

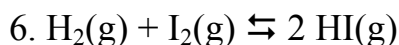
$$K(400 \text{ K}) = \mathbf{1.27 \times 10^9}$$

$$\Delta_r G^\circ(400 \text{ K}) = -RT \ln K(400 \text{ K}) = -(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (400 \text{ K}) \times \ln 1.27 \times 10^9$$

$$= \mathbf{-69.72 \text{ kJ mol}^{-1}}$$

$$5. \quad K = \frac{a_{\text{CO}} a_{\text{H}_2}}{a_{\text{H}_2\text{CO}}} \approx \frac{p_{\text{CO}} p_{\text{H}_2}}{p_{\text{H}_2\text{CO}}} = \frac{x_{\text{CO}} p x_{\text{H}_2} p}{x_{\text{H}_2\text{CO}} p} = \frac{x_{\text{CO}} x_{\text{H}_2}}{x_{\text{H}_2\text{CO}}} p = K_x p$$

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%**.



	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.

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

This equation reduces to the following quadratic equation:

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

Use the quadratic formula to solve this equation:

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

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 : $0.3 - 0.2933 = \mathbf{0.0067}$; I_2 : $0.4 - 0.2933 = \mathbf{0.1067}$; HI : $0.2 + 2 \times 0.2933 = \mathbf{0.7866}$ (all in mol)

7. $\text{A} + 3 \text{B} \rightleftharpoons 2 \text{C}$

	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	$\frac{1 - \xi}{2(2 - \xi)} p$	$\frac{3(1 - \xi)}{2(2 - \xi)} p$	$\frac{\xi}{2 - \xi} p$

$$K = \frac{(p_{\text{C}}/p^\ominus)^2}{(p_{\text{A}}/p^\ominus)(p_{\text{B}}/p^\ominus)^3} = \frac{\left(\frac{\xi}{2 - \xi}\right)^2}{\left(\frac{1 - \xi}{2(2 - \xi)}\right)\left(\frac{3(1 - \xi)}{2(2 - \xi)}\right)^3} = \frac{16(2 - \xi)^2 \xi^2}{27(1 - \xi)^4} \left(\frac{p^\ominus}{p}\right)^2$$

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

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

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

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

