Textbook Review questions from Chapter 14:
pg .p.621-625 #63, 66, 68b, 72, 78, 81, 86, 88*, 92(b,c), 98, 103, 107
*For #88, *make initial moles $H_2 = 0.984$ to be equal to initial moles I_2*

63   **What is missing from the statement, "The equilibrium constant of a reacting mixture of solid NH_4Cl and gaseous NH_3 and N_2 is 0.316."**
(i)   The temperature of the system is not given.
(ii) It is not stated whether the equilibrium constant is K_p or K_c
(iii) A balanced equation is not given.

66   **Baking soda decomposes as follows: $NaHCO_3(s) \rightleftharpoons Na_2CO_3(s) + CO_2(g) + H_2O(g)$. Would we obtain more CO_2 and H_2O by adding extra baking soda to the reaction mixture in …**
The equilibrium expression for this system is given by:

$$K_p = P_{CO_2}P_{H_2O}$$

(a) a closed vessel?   In a closed vessel the decomposition will stop when the product of the partial pressures of CO_2 and H_2O equals K_p. Adding more sodium bicarbonate will have **no effect**.

(b) an open vessel?   In an open vessel, $CO_2(g)$ and $H_2O(g)$ will escape from the vessel, and the partial pressures of CO_2 and H_2O will never become large enough for their product to equal K_p. Therefore, equilibrium will never be established. Adding more sodium bicarbonate will result in the production of **more CO_2 and H_2O**.

68   **The equilibrium constant K_p for the reaction $2\ H_2O(g) \rightleftharpoons 2\ H_2(g) + O_2(g)$ is 2×10^{-42} at 25°C.**
(b) Why can H_2 and O_2 be kept together indefinitely with no change?
Because of a very large activation energy, the reaction of hydrogen with oxygen is infinitely slow without a catalyst or an initiator. The action of a single spark on a mixture of these gases results in the explosive formation of water.

72   **Consider the reaction $2\ NO\ (g) + O_2\ (g) \rightleftharpoons 2\ NO_2\ (g)$. At 430°C an equilibrium mixture contains 0.020 mol O_2, 0.040 mol NO, and 0.96 mol NO_2. <u>Determine K_P</u> if $P_{Total} = 0.20$ atm.**
Total number of moles of gas is:

$$0.020 + 0.040 + 0.96 = 1.02 \text{ mol of gas}$$

Calculate the partial pressure of each component from the mole fraction and the total pressure.

$$P_{NO} = X_{NO}P_T = \frac{0.040}{1.02} \times 0.20\,atm = 0.0078\ atm$$

$$P_{NO_2} = X_{NO_2}P_T = \frac{0.96}{1.02} \times 0.20\,atm = 0.19\ atm$$
$$P_{O_2} = X_{O_2}P_T = \frac{0.020}{1.02} \times 0.20\,atm = 0.0039\ atm$$

$$K_p = \frac{P^2_{NO_2}}{P^2_{NO}P_{O_2}} = \frac{(0.19)^2}{(0.0078)^2(0.0039)} = \mathbf{1.5 \times 10^5}$$

78   **6.75 g SO_2Cl_2 is placed in a 2.00-L flask. At 648 K, there is 0.0345 mol SO_2 present. Calculate K_c for the reaction SO_2Cl_2 (g) $\rightleftharpoons$ SO_2 (g) + Cl_2 (g).**

$$[SO_2Cl_2]_0 = \frac{6.75 \text{ g } SO_2Cl_2 \times \dfrac{1 \text{ mol } SO_2Cl_2}{135.0 \text{ g } SO_2Cl_2}}{2.00 \text{ } L} = 0.0250 \text{ } M$$

At equilibrium, $[SO_2] = \dfrac{0.0345 \text{ } mol}{2.00 \text{ } L} = 0.01725 \text{ } M$

Since there is a 1:1 mole ratio between SO_2 and SO_2Cl_2, the concentration of SO_2 at equilibrium (0.01725 M) equals the concentration of SO_2Cl_2 reacted.

	$SO_2Cl_2(g)$	$\rightleftharpoons$	$SO_2(g)$	+	$Cl_2(g)$
Initial (M):	**0.0250**		0		0
Change (M):	−0.01725		+0.01725		+0.01725
Equilibrium (M):	0.00775		**0.01725**		0.01725

$$K_c = \frac{[SO_2][Cl_2]}{[SO_2Cl_2]} = \frac{(0.0173)(0.0173)}{(0.00775)} = \mathbf{3.86 \times 10^{-2}}$$

81   **Eggshells are formed by the process Ca^{2+} (aq) + CO_3^{2-} (aq) $\rightleftharpoons$ $CaCO_3$ (s). The carbonate ion comes from CO_2 formed in metabolism. Why are eggshells thinner in summer?**
- Panting decreases the concentration of CO_2 because CO_2 is exhaled during respiration.
- This decreases the concentration of carbonate ions, shifting the equilibrium to the left. Less $CaCO_3$ is produced.
- Two possible solutions would be either to cool the chickens' environment or to feed them carbonated water.

88   **The equilibrium constant, K_C for the reaction H_2 (g) + I_2 (g) $\rightleftharpoons$ 2 HI (g) is 54.3 at 430°C. Initially there are 0.984 mol H_2, 0.984 mol I_2 and 0.886 mol HI in a 2.40-L flask. What are the equilibrium concentrations?**

$$[H_2]_0 = [I_2]_0 = \frac{0.984 \text{ } mol}{2.40 \text{ } L} = 0.410 \text{ } M \text{ ; } [HI]_0 = \frac{0.886 \text{ } mol}{2.40 \text{ } L} = 0.369 \text{ } M$$

$$Q_c = \frac{[HI]_0^2}{[H_2]_0[I_2]_0} = \frac{(0.369)^2}{(0.410)(0.410)} = 0.81$$

$Q_c < K_c$. The equilibrium will shift to the right, decreasing the concentrations of H_2 and I_2 and increasing the concentration of HI.

	H_2	+	I_2	$\rightleftharpoons$	2 HI
Initial (M):	0.410		0.410		0.369
Change (M):	−x		−x		+2x
Equilibrium (M):	(0.410 − x)		(0.410 − x)		(0.369 + 2x)

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{(0.369 + 2x)^2}{(0.410 - x)^2} = 54.3;$$

Taking the square root of both sided gives $\dfrac{(0.369 + 2x)}{(0.410 - x)} = 7.37$ and $x = 0.283 \text{ } M$.

$$[H_2] = [I_2] = (0.410 - 0.283) \text{ } M = \mathbf{0.127 \text{ } M}$$
$$[HI] = [0.369 + 2(0.283)] \text{ } M = \mathbf{0.935 \text{ } M}$$

92 The equilibrium constant K_C for the reaction $N_2\ (g) + 3\ H_2\ (g) \rightleftharpoons 2\ NH_3\ (g)$ is 1.2 at 375°C.

K_C **for the reaction is:** $K_c = \dfrac{[NH_3]^2}{[N_2][H_2]^3} = 1.2$

(b) **What is the value of K_C for the reaction $2\ NH_3\ (g) \rightleftharpoons N_2\ (g) + 3\ H_2\ (g)$?**

$K_{forward} = \left(K_{reverse}\right)^{-1}$, so $K_c' = \left(1.2\right)^{-1} = \mathbf{0.83}$

(c) **What is the value of K_C for the reaction $\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \rightleftharpoons NH_3(g)$?**

The reaction is equivalent to $\frac{1}{2}[N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)]$, so

$K_c' = (K_c)^{\frac{1}{2}} = \sqrt{1.2} = \mathbf{1.1}$

98 **Photosynthesis can be represented as: $6\ CO_2\ (g) + 2\ H_2O\ (l) \rightleftharpoons C_6H_{12}O_6\ (s) + 6\ O_2\ (g)$ $\Delta H° = 2801$ kJ/mol. How is equilibrium affected if:**

(a) **partial pressure of CO_2 is increased:** shifts to right to consume added reactant

(b) **O_2 is removed from the mixture:** shifts to right to replace depleted product

(c) **$C_6H_{12}O_6$ (glucose) is removed from the mixture:** no change (as long as some glucose remains)

(d) **more water is added:** no change because water is a pure liquid

(e) **a catalyst is added:** no change

(f) **temperature is decreased:** shifts to left (decrease in T favors the *exothermic* direction)

103 **Consider the system $3\ A \rightleftharpoons B$. Sketch the changes in [A] and [B] over time if one assumes that $[B]_{eq} > [A]_{eq}$:**
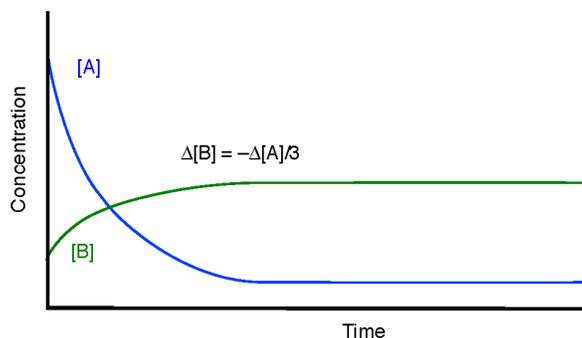
a) **Initially only A is present**
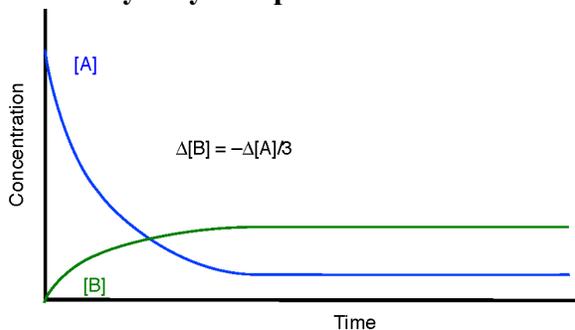
(b) **Initially only B is present.**
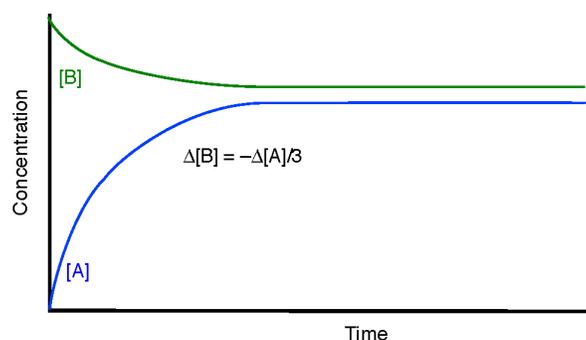
(c) **Initially A and B are both present with $[A]_0 > [B]_0$.**

107   **For the reaction A $\rightleftharpoons$ B represented by either the left or right energy diagram, explain:**

Reaction progress   Reaction progress

(a) **How would a catalyst affect the forward and reverse rates of the reaction?** A catalyst speeds up the rates of the forward and reverse reactions to the same extent.

(b) **How would a catalyst affect the energies of the reactant and product?** A catalyst would not change the energies of the reactant and product.

(c) **How would an increase in T affect the equilibrium constant?** The first reaction is exothermic. Raising the temperature would favor the reverse reaction, increasing the amount of reactant and decreasing the amount of product at equilibrium. The equilibrium constant, K, would decrease. The second reaction is endothermic. Raising the temperature would favor the forward reaction, increasing the amount of product and decreasing the amount of reactant at equilibrium. The equilibrium constant, K, would increase.

(d) **If the only effect of a catalyst is to lower the activation energies of the forward and reverse reactions, show that the equilibrium constant remains unchanged if a catalyst is added.** A catalyst lowers the activation energy for the forward and reverse reactions to the same extent. Adding a catalyst to a reaction mixture will simply cause the mixture to reach equilibrium sooner. The same equilibrium mixture could be obtained without the catalyst, but we might have to wait longer for equilibrium to be reached. If the same equilibrium position is reached, with or without a catalyst, then the equilibrium constant is the same.