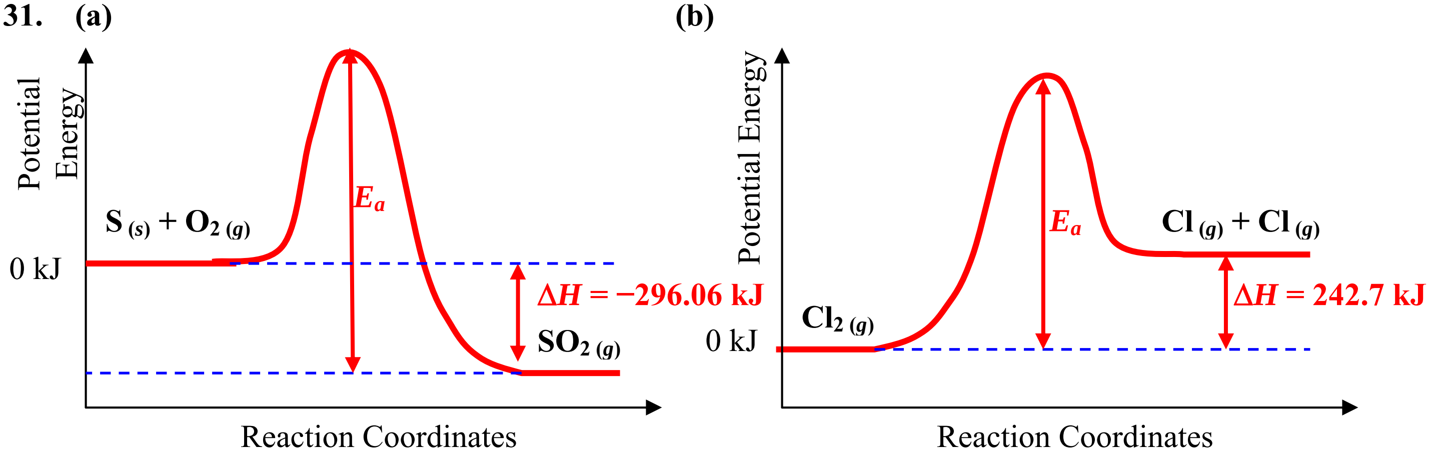
Unit 5: Chemical Kinetics and Equilibrium

Chapter 14: Chemical Kinetics (pg. 489 to 493)

27. Activation energy is the amount of energy needed to overcome for the products to form. All reactions have some kind of activation energy. The higher is the activation energy, the slower the reaction rate.

30. Methane and oxygen gas mixture does not react spontaneous in a hydrocarbon combustion because the molecules do not have enough energy to initiate the reaction. In order for combustion to occur, the molecules must attain enough energy such that the resulting collision with break their existing covalent bonds and form new bonds.

31.



49. A catalyst increase the rate of reaction by providing an alternate reaction pathway and thereby reducing the amount of activation energy to initialize the reaction.

50. A catalyst does not get consume in a reaction, which means it gets recycled at the end of the reaction for more reactants

51. Yes, one can increase the rate of reaction without changing the temperature by adding a suitable catalyst.

52. Heterogeneous catalysts are catalysts that exist in different phases compared to the reactants. Metal alloys such as iron with aluminium oxide and potassium oxides and pure platinum are solid alloys commonly used for the production of ammonia from nitrogen and hydrogen gases. Homogeneous catalysts are catalysts that exist in the same phase as the reactants. An acid can be used to speed up the reaction of ethyl acetate and water into acetic acid and ethanol.

75 **(a)** A catalyst works by changing the reaction energy profile, thus lowering the activation energy.
(c) A catalyst does not change the enthalpy of reaction

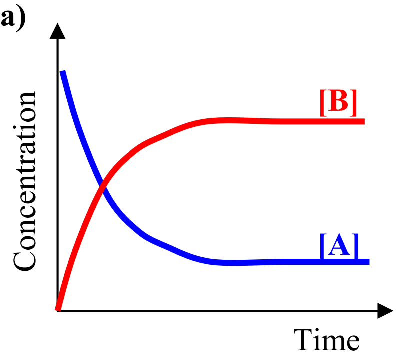
Chapter 15: Chemical equilibrium (pg. 520 to 525)

1. A chemical equilibrium is a state where the rate of the forward reaction is the same as the reverse reaction. A dynamic equilibrium emphasizes that even if the concentrations of reactants and products remain constant at equilibrium, molecules do react with in the forward and reverse direction. Hence, they are not static, but dynamic. An example of a dynamic equilibrium at water's boiling point, the rate of vaporization is the same as the rate of condensation $H_2O_{(l)} \rightleftharpoons H_2O_{(g)}$. Another example is the equilibrium system between $NO_{2\,(g)}$, a brown gas, and its dimer form $N_2O_{4\,(g)}$, a colourless gas, $2\,NO_{2\,(g)} \rightleftharpoons N_2O_{4\,(g)}$.

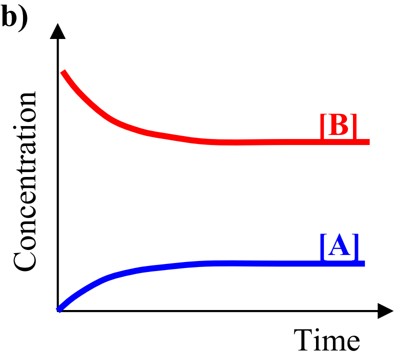
2. A physical equilibrium is an equilibrium due to a physical change such as phase changes or dissolving ionic compounds. $H_2O_{(l)} \rightleftharpoons H_2O_{(g)}$ and $Ca(OH)_{2\,(s)} \rightleftharpoons Ca^{2+}{}_{(aq)} + SO_4^{2-}{}_{(aq)}$ are examples of physical equilibrium. A chemical equilibrium has to do with an equilibrium involving a chemical change. Examples of chemical equilibrium are $2\,NO_{2\,(g)} \rightleftharpoons N_2O_{4\,(g)}$ and $N_{2\,(g)} + H_{2\,(g)} \rightleftharpoons NH_{3\,(g)}$.

3. The study of equilibrium allows us to predict the concentrations or the pressures of all chemicals in the system. Therefore, it enables us to manipulate conditions such as temperature and pressure to maximize or minimize their yields.

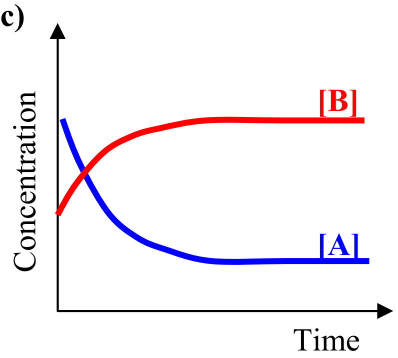
4. **(a)**



(b)



(c)



5. Homogeneous equilibrium is an equilibrium system where all the chemical species are in the same phases. Some examples of homogeneous equilibriums are $N_{2\,(g)} + H_{2\,(g)} \rightleftharpoons NH_{3\,(g)}$ and $CH_3COOH_{(aq)} \rightleftharpoons H^+_{(aq)} + CH_3COO^-_{(aq)}$. Heterogeneous equilibrium is an equilibrium system where not all the chemical species are in the same phases. Some examples of heterogeneous equilibriums are $AgCl_{(s)} \rightleftharpoons Ag^+_{(aq)} + Cl^-_{(aq)}$ and $NH_4Cl_{(s)} \rightleftharpoons NH_{3\,(g)} + HCl_{(g)}$.

6. K_c represents the equilibrium constant when all the quantities used are molar concentrations in mol/L. K_P represents the equilibrium constant when all the quantities used are partial pressures in atm.

7. **(a)** $K_c = \dfrac{[CO]^2[O_2]}{[CO_2]^2}$ $K_P = \dfrac{P_{CO}^2 \bullet P_{O_2}}{P_{CO_2}^2}$ **(b)** $K_c = \dfrac{[O_3]^2}{[O_2]^3}$ $K_P = \dfrac{P_{O_3}^2}{P_{O_2}^3}$

(c) $K_c = \dfrac{[COCl_2]}{[CO][Cl_2]}$ $K_P = \dfrac{P_{COCl_2}}{P_{CO} \bullet P_{Cl_2}}$ **(d)** $K_c = \dfrac{[CO][H_2]}{[H_2O]}$ $K_P = \dfrac{P_{CO} \bullet P_{H_2}}{P_{H_2O}}$

(e) $K_c = \dfrac{[H^+][HCOO^-]}{[HCOOH]}$ **(d)** $K_c = [O_2]$ $K_P = P_{O_2}$

9. **(a)** $K_c = \dfrac{[NH_3]^2}{[NO_2]^2[H_2]^7}$ $K_P = \dfrac{P_{NH_3}^2}{P_{NO_2}^2 \bullet P_{H_2}^7}$ **(b)** $K_c = \dfrac{[SO_2]^2}{[O_2]^3}$ $K_P = \dfrac{P_{SO_2}^2}{P_{O_2}^3}$

(c) $K_c = \dfrac{[CO]^2}{[CO_2]}$ $K_P = \dfrac{P_{CO}^2}{P_{CO_2}}$ **(b)** $K_c = \dfrac{[C_6H_5COO^-][H^+]}{[C_6H_5COOH]}$

11. $K_c = \dfrac{[B]}{[A]}$

(1) With $K_c = 10$, products are favored at equilibrium. Because the coefficients for both A and B are one, we expect the concentration of B to be 10 times that of A at equilibrium. Choice **(a)** is the best choice with 10 B molecules and 1 A molecule.

(2) With $K_c = 0.10$, reactants are favored at equilibrium. Because the coefficients for both A and B are one, we expect the concentration of A to be 10 times that of B at equilibrium. Choice **(d)** is the best choice with 10 A molecules and 1 B molecule.

You can calculate K_c in each case without knowing the volume of the container because the mole ratio between A and B is the same. Volume will cancel from the K_c expression. Only moles of each component are needed to calculate K_c.

13. K' or $K_{\text{reverse}} = 2.40 \times 10^{33}$

15. $K_P = 1.76 \times 10^{20}$

17. $K_P = 0.051$

19. $K_P = 3.2 \times 10^2$

21. $Q_P = 0.140$ and K_P given is 1.05. Since the calculated value of Q_P is less than K_P for this system, the system will change in a way to increase Q_P until it is equal to K_P. To achieve this, the pressures of PCl_3 and Cl_2 must ***increase***, and the pressure of PCl_5 must ***decrease***.

23. $K_c = 6.3 \times 10^{-4}$

25. $K_P = 9.3 \times 10^{-3}$; $K_P = 3.8 \times 10^{-4}$

27. Reaction quotient (Q_c or Q_P) is a number equal to the ratio of the products' concentrations or pressures to reactants' concentrations or pressures, each raised to the power of its stoichiometric coefficient ***at some point other than equilibrium***. This is different than the Equilibrium constant (K_c or K_P) where the concentrations and pressures are ***already at equilibrium***.

28. **i.** Set up the ICE box and find the initial concentrations and partial pressures of all chemical species.
ii. Find the reaction quotient (Q) if necessary and compare to the equilibrium constant (K).
iii. Label $+x$ or $-x$ in the Change (or C) row, according to the conclusion of the last step. Remember to use mole ratios.
iv. Write down the equilibrium expression of the equilibrium concentrations or partial pressures of all chemical species.
v. Solve the expression and x.
vi. Substitute x back into the expressions and find the equilibrium concentrations or partial pressures.

29. Initially, the total pressure is (0.350 + 0.762) atm or 1.112 atm. As the reaction progresses from left to right toward equilibrium there will be a decrease in the number of moles of molecules present. (Note that 2 moles of SO_2 react with 1 mole of O_2 to produce 2 moles of SO_3, or, at constant pressure, three atmospheres of reactants forms two atmospheres of products.) Since pressure is directly proportional to the number of molecules present, at equilibrium the total pressure will be less than 1.112 atm.

31. 0.173 mol H_2

33. $[H_2]_{eq} = [Br_2]_{eq} = 1.80 \times 10^{-4}$ M ; [HBr] = 0.267 M

35. $P_{COCl_2} = 0.408$ atm ; $P_{CO} = P_{Cl_2} = 0.352$ atm

37. $P_{CO} = 1.96$ atm ; $P_{CO_2} = 2.54$ atm

39. Le Châtelier's Principle states that if an external stress is applied to a system at equilibrium, the system will adjust itself in such as way as to partially offset the stress. When we study an equilibrium system, we can create a condition where the system "thinks" there are not enough products. Hence, the system constantly shifts to the right until the yields are maximized.

40. Because the equilibrium system between a substances liquid phase and its vapour phase is endothermic ($X_{(l)} + \text{heat} \rightleftharpoons X_{(g)}$), an increase in temperature is similar to increase in concentration of the reactant. This causes the system to compensate by shifting towards the product side, and more gas is produced. The result of more gas increases the vapour pressure of the system.

41. The four factors that can shift the position of equilibrium are concentrations, pressures, volumes, and temperature. Of these, only temperature can change the equilibrium constant, K, because its value is temperature dependent.

42. The position of equilibrium is the relative amount of products and reactants when the system reaches a dynamic equilibrium state. If $K > 1$, there are more products than reactants at equilibrium, and we say the system favours the product side. If $K < 1$, there are less products than reactants at equilibrium, and we say the system favours the reactant side. An addition of catalyst merely speeds up the reaction. That is, to reach the equilibrium state faster. It does not affect the amounts of reactants and products at equilibrium and therefore, a catalyst does not affect the equilibrium position or the value of K.

43. **(a)** Addition of more $Cl_{2\,(g)}$ (a reactant) would shift the position of equilibrium to the **right**.
(b) Removal of $SO_2Cl_{2\,(g)}$ (a product) would shift the position of equilibrium to the **right**.
(c) Removal of $SO_{2\,(g)}$ (a reactant) would shift the position of equilibrium to the **left**.

45. **(a)** This reaction is endothermic (use Hess's Law to add the chemical equations and ΔH's). An increase in temperature favours an endothermic reaction, so the equilibrium constant should become **larger**.

(b) This reaction is exothermic. Such reactions are favored by decreases in temperature. The magnitude of K_c should **decrease**.

(c) In this system heat is neither absorbed nor released. A change in temperature should have **no effect** on the magnitude of the equilibrium constant.

47. **(a)** A pressure increase will favour the forward reaction that decreases the total number of moles of gas. The equilibrium should shift to the **right**. That is, more I_2 will be produced at the expense of I.

(b) If the concentration of I_2 is suddenly altered, the system is no longer at equilibrium. Evaluating the magnitude of the reaction quotient Q_c allows us to predict the direction of the resulting equilibrium shift. The reaction quotient for this system is $Q_c = \frac{[I_2]}{[I]^2}$. Increasing the concentration of I_2 will increase Q_c. The equilibrium will be reestablished in such a way that Q_c is again equal to the equilibrium constant. More I will form. The system shifts to the **left** to establish equilibrium.

(c) The forward reaction is exothermic. A decrease in temperature will shift the system to the **right** to reestablish equilibrium.

49. **(a)** Increasing the temperature favors the endothermic reaction so that the concentrations of SO_2 and O_2 will increase while that of SO_3 will decrease.

(b) Increasing the pressure favors the reaction that decreases the number of moles of gas. The concentration of SO_3 will increase.

(c) Increasing the concentration of SO_2 will lead to an increase in the concentration of SO_3 and a decrease in the concentration of O_2.

(d) A catalyst has no effect on the position of equilibrium.

(e) Adding an inert gas at constant volume has no effect on the position of equilibrium.

51. **(a)** If helium gas is added to the system without changing the pressure or the temperature, the volume of the container must necessarily be increased. This will decrease the partial pressures of all the reactants and products. A pressure decrease will favor the reaction that increases the number of moles of gas. The position of equilibrium will shift to the **left**.

(b) If the volume remains unchanged, the partial pressures of all the reactants and products will remain the same. The reaction quotient, Q_c, will still equal the equilibrium constant, and there will be **no change** in the position of equilibrium.