

Guide to Chapter 13. Chemical Equilibrium

We will spend five lecture days on this chapter. During the first class meeting we will focus on how kinetics makes a segue into equilibrium. We will learn how to write equilibrium constants two different ways, and learn how to interpret equilibrium constants. Next we will do some equilibrium calculations, using equilibrium concentrations to determine equilibrium constants and visa versa. You will become adept at setting up and using "ICE" tables. We'll discuss "mass action expressions" that let us understand what needs to happen in order to get to equilibrium. We will spend time with LeChâtelier's principle end the chapter the way we started: tying kinetics and equilibrium together.

Read the introductory paragraph to Chapter 13.

Read Section 13.1 The Equilibrium State.

Learning Objective 1: Know how reaction situations described by kinetics eventually segue into equilibrium situations

Do the following end-of-chapter problem: 28

Problem Club Question A (ACS Style): Which is true, by definition, for a system that has reached a state of chemical equilibrium?

- (A) *The substance having the smaller volume has a tendency to form at the expense of the other substances.*
- (B) *No further reaction occurs in either direction.*
- (C) *The concentrations of reactants and products are necessarily equal.*
- (D) *The opposing reactions have equal velocities.*
- (E) *The total mass of the products is equal to the total mass of the reactants.*

Answer: D

Read Sections 13.2 – 13.4: Section 13.2. The equilibrium constant, K_c ; Section 13.3 The equilibrium constant, K_p ; and Section 13.4 Heterogeneous equilibria.

Learning Objective 2: Be able to write the equilibrium expressions, K_c , for a given balanced chemical reaction involving homogeneous equilibrium.

Learning Objective 3: Be able to write the equilibrium expressions, K_c , for a given balanced chemical reactions involving heterogeneous equilibrium

Learning Objective 4: Be able to write the equilibrium expressions, K_p , for a given balanced chemical reaction involving homogeneous equilibrium.

Learning Objective 5: Be able to write the equilibrium expressions, K_p , for a given balanced chemical reactions involving heterogeneous equilibrium

Learning Objective 6: Using given concentrations of reactant(s) and product(s), determine the numerical value of the equilibrium constant K_c or K_p for a reaction.

Learning Objective 7: Know the significance of very large (or small) equilibrium constants.

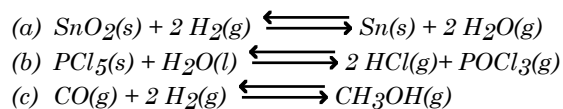
Learning Objective 8: Be able to determine the equilibrium constant expression and the equilibrium constant for situations where chemical equations are reversed, multiplied through by constant coefficients, or added together.

Learning Objective 9: Given K_c , calculate K_p or vice versa.

Do Problems 1 - 4 at the end of Section 13.2, Problems 5 and 6 at the end of Section 13.3 and Problem 7 at the end of section 13.4

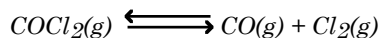
Do the following end-of-chapter problems: 30, 38, 40, 42, 44, 46, 48, 50, 52, 54, 56, 58

Problem Club Question B. Write K_c expressions for



Answer: a. $K_c = [\text{H}_2\text{O}]^2/[\text{H}_2]^2$ b. $K_c = [\text{HCl}]^2/[\text{POCl}_3]$ c. $K_c = [\text{CH}_3\text{OH}]/[\text{H}_2]^2[\text{CO}]$

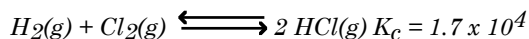
Problem Club Question C. When COCl_2 is heated to 527°C in a reaction vessel, the following equilibrium is attained:



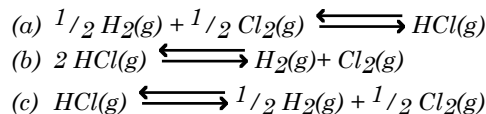
If the equilibrium concentrations are found to be $[\text{CO}] = 0.0456$, $[\text{Cl}_2] = 0.0456$ and $[\text{COCl}_2] = 0.449 \text{ M}$, what is the equilibrium constant?

Answer: 0.00463

Problem Club Question D. Consider the reaction:

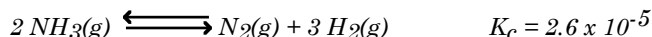


Write the equilibrium expressions, $K_c =$, and determine K_c for each of the following:



Answer: a. 130 b. 5.9×10^{-5} c. 0.0077

Problem Club Question E. Consider the following equilibria at 127°C . Calculate K_p for this reaction.



Answer: 0.0280

Problem Club Question F (ACS Style): Answer: D

Problem Club Question G (ACS Style): Answer: E

Read Sections 13.5 Using the equilibrium constant.

Learning Objective 10: Use the reaction quotient (Q) to determine if a reaction mixture is at equilibrium. Predict the direction a reaction will shift by comparing the reaction quotient (Q) with K_c or K_p .

Learning Objective 11: Given sufficient data concerning initial or equilibrium concentrations of reactants and/or products determine the equilibrium concentrations of each substance in the balanced reaction and the value of K_c .

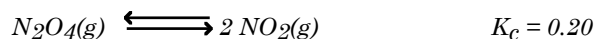
Learning Objective 12: Given sufficient data concerning initial or equilibrium partial pressures of gaseous reactants and/or products determine the equilibrium partial pressures of each substance in the balanced reaction and the value of K_p .

Learning Objective 13: Given the equilibrium constant, K_c , and information concerning the concentration (initial or equilibrium) of reactants/products, calculate the equilibrium concentration of each species in a balanced equilibrium reaction.

Do Problems 8 - 15 embedded within this big section.

Do the following end-of-chapter problems: 60, 62, 64, 66, 68, 70, 72, 74, 76, 94, 96, 98, 100, 106

Problem Club Question H. Consider the reaction below along with the equilibrium constant given.



Suppose that $[N_2O_4] = 0.730 M$ at equilibrium. Calculate the concentration of NO_2 at equilibrium. As in most of these problems, begin by writing the equilibrium expression, K_c .

Answer: 0.382

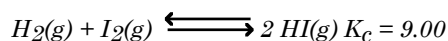
Problem Club Question I. Consider the equilibrium:



If 0.070 moles of NO were placed in a 1.0 L flask and allowed to reach equilibrium, what is the equilibrium concentration of each gas? Hint: Make an "ICE" table.

Answer: $[N_2] = 0.0315$ $[O_2] = 0.0315$ $[NO] = 0.00704$

Problem Club Question J. Consider the equilibrium:



Hydrogen, iodine and HI were placed in a flask in order that the initial concentrations were $[H_2] = 2 M$, $[I_2] = 4 M$, and $[HI] = 1.5 M$. Determine if the system is at equilibrium. If not, which direction must it shift in order to attain equilibrium? Start with the Q_c expression.

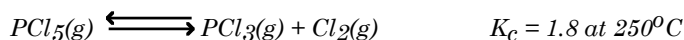
Answer: $Q_c = 0.28$ so reaction must shift right.

Problem Club Question K. For which value for K will the equilibrium mixture consist almost entirely of reactants?

- A. 1×10^{-12} B. 0.012 C. 1.5 D. 19 E. 3×10^7

Answer: A

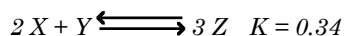
Problem Club Question L. Consider the reaction:



A 1.5 mol sample of PCl_5 is injected into a 0.50-L reaction vessel. Calculate the concentration of each gas at equilibrium.

Answer: $[PCl_5] = 1.41 M$; $[PCl_3] = 1.59 M$; $[Cl_2] = 1.59 M$

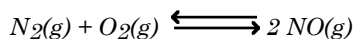
Problem Club Question M. For the all-gas system:



Starting with 0.90 M concentrations of X and Y , it was found that the equilibrium concentration of X was 0.60 M. What is $[Z]$ at equilibrium?

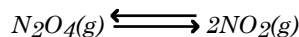
Answer: 0.45

Problem Club Question N. Suppose 2.00 mol NO were placed in a 1.0-L flask at 2273 K. At equilibrium, 0.863 mol N_2 and 0.863 mol O_2 are present. What is K_c for the reaction at this temperature?



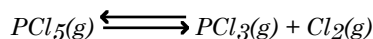
Answer: 0.10

Problem Club Question O. At 70°C , $K_c = 0.090$ for the equilibrium given below. If at equilibrium, $\text{N}_2\text{O}_4 = 3.22\text{ M}$, what is the molar concentration of NO_2 ?



Answer: 0.538

Problem Club Question P. The value of K_c for the equilibrium



is 0.042 at 250°C . If 0.20 mol PCl_3 0.20 mol Cl_2 and 0.50 mol PCl_5 were mixed in a 5.0 L container, which direction, if either, will the reaction shift in order to establish equilibrium?

Answer: shift right

Problem Club Question Q (ACS Style): Answer: C

Problem Club Question R (ACS Style): Answer: D

Problem Club Question S (ACS Style): Answer: B

Problem Club Question T (ACS Style): Answer: C

Problem Club Question U (ACS Style): Answer: D

Problem Club Question V (ACS Style): Answer: B

Read Sections 13.6 Factors that alter the composition of an equilibrium mixture and Section 13.7. Altering an equilibrium mixture: Changes in concentration

Learning Objective 14: Use Le Châtelier's Principle to qualitatively predict the direction the equilibrium will shift (right or left) when a change in concentration has been introduced.

Do Problem 16 at the end of this section.

Do the following end-of-chapter problem: 78

Problem Club Question W. Consider the equilibrium: $\text{H}_2(\text{g}) + \text{CO}_2(\text{g}) \rightleftharpoons \text{H}_2\text{O}(\text{g}) + \text{CO}(\text{g})$

Predict the qualitative effect on the equilibrium concentration of each gas by an increase in the pressure of water.

Answer: H_2 and CO_2 increases; CO decreases

Read Sections 13.8. Altering an equilibrium mixture: Changes in pressure and volume

Learning Objective 14: Use Le Châtelier's Principle to qualitatively predict the direction the equilibrium will shift (right or left) when a change in pressure has been introduced.

Learning Objective 14: Use Le Châtelier's Principle to qualitatively predict the direction the equilibrium will shift (right or left) when a change in volume has been introduced.

Do Problems 17 and 18 at the end of this section.

Do the following end-of-chapter problems: 80

Problem Club Question X. For the system $\text{A}(\text{g}) \rightleftharpoons \text{B}(\text{g}) + 2\text{C}(\text{g})$, the K_c is 8.0×10^{16} . Which of the following statements is possible?

- A. The equilibrium $[B]$ and $[C]$ is much greater than $[A]$.
- B. Increasing the pressure will decrease K_c .
- C. Adding A will increase K_c
- D. Increasing the volume container will increase K_c

Answer: A

Problem Club Question Y. Which of the following would shift left if the container volume were decreased?
Shift right? Not shift?

- (a) $N_2(g) + O_2(g) \rightleftharpoons 2 NO(g)$
- (b) $2 NO(g) + O_2(g) \rightleftharpoons 2 NO_2(g)$
- (c) $2 HI(g) \rightleftharpoons H_2(g) + I_2(g)$
- (d) $2 HI(g) \rightleftharpoons H_2(g) + I_2(s)$

Answer: a. no shift b. shift right c. no shift

Problem Club Question Z. For which of the equilibria in the previous question is $K_c = K_p$?

Answer: a and c

Problem Club Question AA (ACS Style): Answer: D

Read Sections 13.9. Altering an equilibrium mixture: Changes in temperature.

Learning Objective 14: Use Le Châtelier's Principle to qualitatively predict the direction the equilibrium will shift (right or left) when a change in temperature has been introduced.

Learning Objective 26: Qualitatively predict how K_c or K_p will change (increase or decrease) when the temperature is changed.

Do Problems 19 - 21 at the end of this section.

Do the following end-of-chapter problems: 34, 36, 82

Problem Club Question BB. Consider the reaction:

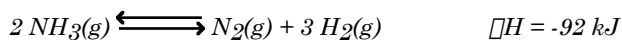


Which way will the equilibrium shift by:

- (a) an increase in temperature
- (b) an increase in the size of the reaction container's volume
- (c) an increase in the pressure of hydrogen
- (d) a decrease in the pressure of methane
- (e) addition of more carbon

Answer: a. L b. L c. R d. R d. right e. no effect

Problem Club Question CC. Consider the equilibrium:



The concentration of NH_3 may be increased by: (possibly more than one of the following!)

- A. increasing the pressure in the container.
- B. decreasing the pressure in the container
- C. adding an inert gas such as argon
- D. increasing the temperature
- E. adding hydrogen

Answer: a. Y b. N c. N d. Y e. Y

Problem Club Question DD. (ACS-Style) Answer: C

Problem Club Question EE (ACS Style): Answer: A

Problem Club Question FF (ACS Style): Answer: C

Read Sections 13.10. The effect of a catalyst on equilibrium.

Learning Objective 14: Use Le Châtelier's Principle to qualitatively predict the direction the equilibrium will shift (right or left) when a catalyst has been added.

Do Problem 22 at the end of this section.

Do the following end-of-chapter problems: 86

Problem Club Question GG. Which of the following will be affected by the addition of a catalyst::

- (a) K_c (b) K_p (c) the rate constant

Answer: C

Problem Club Question HH. The only stress to an equilibrium resulting in a change to the value of the equilibrium constant is:

- A. a change in temperature
- B. a change in the pressure
- C. an addition of a reactant
- D. the addition of a catalyst
- E. the removal of a product

Answer: A

Read Sections 13.11. The link between chemical equilibrium and chemical kinetics.

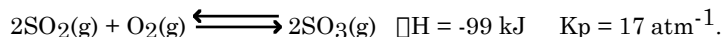
Learning Objective 25: Given a concentration vs. time plot, identify regions where kinetic measurements and equilibrium calculations can be obtained.

Learning Objective 26: Determine K_c or K_p from given data concerning the forward and reverse reaction rates.

Do Problem 23 at the end of this section.

Do the following end-of-chapter problems: 88, 90, 92

Problem Club Questions II. Consider the following equilibrium in order to answer the next five questions:



Problem Club Question JJ. General Questions.

- a. What will happen to K_p if the temperature is increased?
- b. Suppose a sample of SO_3 is placed in an empty flask and allowed to come to equilibrium. If the equilibrium pressure of SO_3 is 1 atm, then are the pressures of SO_2 and O_2 greater than or less than 1 atm?
- c. Complete the sentences as it pertains to the above equilibrium: If the container is expanded from 10-L to 20-L, the pressures of all the gases will temporarily (increase/decrease). Immediately after expanding the container volume, the equilibrium constant K_p (increases/decreases/remains unchanged). LeChatelier's Principle predicts that the reaction will (shift left/shift right/not shift) in order to re-establish equilibrium. The change in pressure for SO_2 is (twice/half/same) as that for O_2 .

Answer: a. K_p will decrease; b. both less than 1 atm; c. decrease; remains unchanged; shift left; twice

Problem Club Question KK. Suppose a sample of SO_3 is placed in an empty flask and allowed to come to equilibrium as described in Part 1b above. If the equilibrium pressure of SO_3 is 1 atm, then determine

the equilibrium pressures of SO_2 and O_2 (Answer will have units of atm). Hint: Start by setting up an initial/change/equilibrium table. The initial concentration of SO_3 is not given but you do know the initial concentrations of SO_2 and O_2 from the equilibrium expression. Next, write the equilibrium expression for K_p in terms of the pressure of each gas, P_{SO_2} etc. Also substitute in the values from the table above. OK, ready for something new? Your answer in the previous step should have looked like: $K_p = P_{\text{SO}_3}/P_{\text{SO}_2}P_{\text{O}_2} = 1^2/(2x)^2(x) = 17$. Solve for x by taking the cubed root on your calculator. (If you have never done this, try taking the cubed root of the number: Enter 343, then the y^x button and 0.3333 followed by "="). The answer should be 7. You will be doing many of these in the weeks ahead.) So back to the problem at hand, solve for x and complete the answer to the original question.

Answer: $P_{\text{SO}_2} = 0.490 \text{ atm}$; $P_{\text{O}_2} = 0.245 \text{ atm}$; $P_{\text{SO}_3} = 1.00 \text{ atm}$

Problem Club Question LL. Use the table to determine the original pressure of SO_3

Answer: 1.49 atm

Problem Club Question MM. On graph paper, plot Pressure (atm) on the y-axis and Reaction Time (in minutes) on the x-axis. Using the data and the results that you have determined, plot the concentration of all three gases for this reaction. Assume that it took 2.0 minutes to reach equilibrium.

Answer: The plot should have P_{SO_3} starting at 1.49 atm and decreasing to 1.00 atm at two minutes and horizontal thereafter. The other two gases will start at 0.0 atm and level out at two minutes. The horizontal regions for SO_2 and O_2 reflects their equilibrium concentrations.

Problem Club Question NN. Answer the following questions about the plot in the previous problem.

- Label the kinetics region and the equilibrium region.
- If the temperature were increased, what would happen to the kinetics region?
- Consider ΔH in order to predict which way each equilibrium concentration will change if the temperature is increased.

Answer: a 0-2 minutes is kinetics region where all slopes are non-zero.

b. it would decrease from 2 minutes to some smaller value

c. an increase in temperature will always shift exothermic reactions to the left

Problem Club Question OO (ACS Style): Answer: E