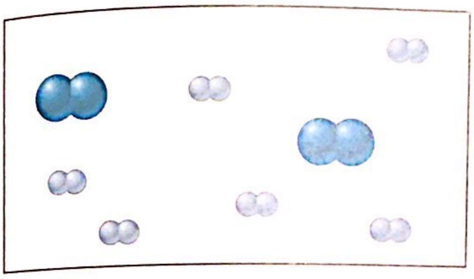
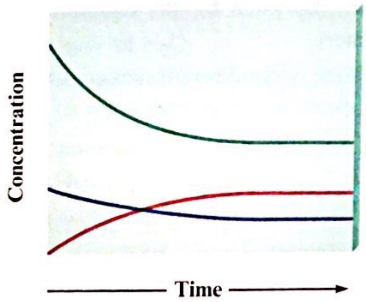
A blue question or exercise number indicates that the answer to that question or exercise appears at the back of this book and a solution appears in the *Solutions Guide*, as found on PowerLecture.

Questions

10. Consider an initial mixture of N_2 and H_2 gases that can be represented as follows:



The gases react to form ammonia gas (NH_3) as represented by the following concentration profile:



a. Label each plot on the graph as N_2, H_2, or NH_3, and explain your answers.

b. Explain the relative shapes of the plots.

c. When is equilibrium reached? How do you know?

11. Consider the following reaction:

$$H_2O(g) + CO(g) \rightleftharpoons H_2(g) + CO_2(g)$$

Amounts of H_2O, CO, H_2, and CO_2 are put into a flask so that the composition corresponds to an equilibrium position. If the CO placed in the flask is labeled with radioactive ^{14}C, will ^{14}C be found only in CO molecules for an indefinite period of time? Explain.

12. Consider the same reaction as in Question 11. In one experiment 1.0 mole of $H_2O(g)$ and 1.0 mole of CO(g) are put into a flask and heated to 350°C. In a second experiment 1.0 mole of $H_2(g)$ and 1.0 mole of $CO_2(g)$ are put into another flask with the same volume as the first. This mixture is also heated to 350°C. After equilibrium is reached, will there be any difference in the composition of the mixtures in the two flasks?

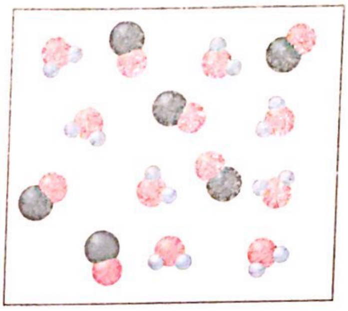
13. Suppose a reaction has the equilibrium constant $K = 1.3 \times 10^8$. What does the magnitude of this constant tell you about the relative concentrations of products and reactants that will be present once equilibrium is reached? Is this reaction likely to be a good source of the products?

14. Suppose a reaction has the equilibrium constant $K = 1.7 \times 10^{-8}$ at a particular temperature. Will there be a large or small amount of unreacted starting material present when this reaction reaches equilibrium? Is this reaction likely to be a good source of products at this temperature?

15. Consider the following reaction at some temperature:

$$H_2O(g) + CO(g) \rightleftharpoons H_2(g) + CO_2(g) \qquad K = 2.0$$

Some molecules of H_2O and CO are placed in a 1.0-L container as shown below.

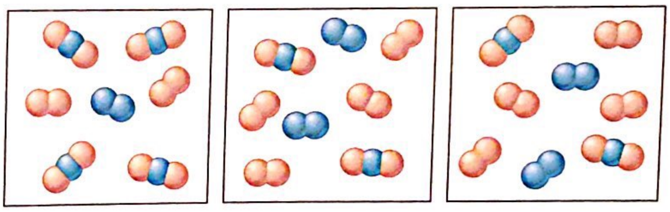


When equilibrium is reached, how many molecules of H_2O, CO, H_2, and CO_2 are present? Do this problem by trial and error—that is, if two molecules of CO react, is this equilibrium; if three molecules of CO react, is this equilibrium; and so on.

16. Consider the following generic reaction:

$$2A_2B(g) \rightleftharpoons 2A_2(g) + B_2(g)$$

Some molecules of A_2B are placed in a 1.0-L container. As time passes, several snapshots of the reaction mixture are taken as illustrated below.



Which illustration is the first to represent an equilibrium mixture? Explain. How many molecules of A_2B reacted initially?

17. Explain the difference between K, K_p, and Q.

18. Consider the following reactions:

$$H_2(g) + I_2(g) \longrightarrow 2HI(g) \quad \text{and} \quad H_2(g) + I_2(s) \longrightarrow 2HI(g)$$

List two property differences between these two reactions that relate to equilibrium.

19. For a typical equilibrium problem, the value of K and the initial reaction conditions are given for a specific reaction, and you are asked to calculate the equilibrium concentrations. Many of these calculations involve solving a quadratic or cubic equation. What can you do to avoid solving a quadratic or cubic equation and still come up with reasonable equilibrium concentrations?

20. Which of the following statements is(are) *true*? Correct the false statement(s).

a. When a reactant is added to a system at equilibrium at a given temperature, the reaction will shift right to reestablish equilibrium.

b. When a product is added to a system at equilibrium at a given temperature, the value of K for the reaction will increase when equilibrium is reestablished.

c. When temperature is increased for a reaction at equilibrium, the value of K for the reaction will increase.

d. When the volume of a reaction container is increased for a system at equilibrium at a given temperature, the reaction will shift left to reestablish equilibrium.

e. Addition of a catalyst (a substance that increases the speed of the reaction) has no effect on the equilibrium position.

Exercises

In this section similar exercises are paired.

The Equilibrium Constant

21. Write the equilibrium expression (K) for each of the following gas-phase reactions.

a. $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$

b. $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

c. $SiH_4(g) + 2Cl_2(g) \rightleftharpoons SiCl_4(g) + 2H_2(g)$

d. $2PBr_3(g) + 3Cl_2(g) \rightleftharpoons 2PCl_3(g) + 3Br_2(g)$

22. Write the equilibrium expression (K_p) for each reaction in Exercise 21.

23. At a given temperature, $K = 1.3 \times 10^{-2}$ for the reaction

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

Calculate values of K for the following reactions at this temperature.

a. $\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \rightleftharpoons NH_3(g)$

b. $2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$

c. $NH_3(g) \rightleftharpoons \frac{1}{2}N_2(g) + \frac{3}{2}H_2(g)$

d. $2N_2(g) + 6H_2(g) \rightleftharpoons 4NH_3(g)$

24. For the reaction

$$H_2(g) + Br_2(g) \rightleftharpoons 2HBr(g)$$

$K_p = 3.5 \times 10^4$ at 1495 K. What is the value of K_p for the following reactions at 1495 K?

a. $HBr(g) \rightleftharpoons \frac{1}{2}H_2(g) + \frac{1}{2}Br_2(g)$

b. $2HBr(g) \rightleftharpoons H_2(g) + Br_2(g)$

c. $\frac{1}{2}H_2(g) + \frac{1}{2}Br_2(g) \rightleftharpoons HBr(g)$

25. For the reaction

$$2NO(g) + 2H_2(g) \rightleftharpoons N_2(g) + 2H_2O(g)$$

it is determined that, at equilibrium at a particular temperature, the concentrations are as follows: $[NO(g)] = 8.1 \times 10^{-3}$ M, $[H_2(g)] = 4.1 \times 10^{-5}$ M, $[N_2(g)] = 5.3 \times 10^{-2}$ M, and $[H_2O(g)] = 2.9 \times 10^{-3}$ M. Calculate the value of K for the reaction at this temperature.

26. At high temperatures, elemental nitrogen and oxygen react with each other to form nitrogen monoxide:

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$$

Suppose the system is analyzed at a particular temperature, and the equilibrium concentrations are found to be $[N_2] = 0.041$ M, $[O_2] = 0.0078$ M, and $[NO] = 4.7 \times 10^{-4}$ M. Calculate the value of K for the reaction.

27. At a particular temperature, a 3.0-L flask contains 2.4 moles of Cl_2, 1.0 mole of NOCl, and 4.5×10^{-3} mole of NO. Calculate K at this temperature for the following reaction:

$$2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g)$$

28. At a particular temperature a 2.00-L flask at equilibrium contains 2.80×10^{-4} mole of N_2, 2.50×10^{-5} mole of O_2, and 2.00×10^{-2} mole of N_2O. Calculate K at this temperature for the reaction

$$2N_2(g) + O_2(g) \rightleftharpoons 2N_2O(g)$$

If $[N_2] = 2.00 \times 10^{-4}$ M, $[N_2O] = 0.200$ M, and $[O_2] = 0.00245$ M, does this represent a system at equilibrium?

29. The following equilibrium pressures at a certain temperature were observed for the reaction

$$2NO_2(g) \rightleftharpoons 2NO(g) + O_2(g)$$

$$P_{NO_2} = 0.55 \text{ atm}$$
$$P_{NO} = 6.5 \times 10^{-5} \text{ atm}$$
$$P_{O_2} = 4.5 \times 10^{-5} \text{ atm}$$

Calculate the value for the equilibrium constant K_p at this temperature.

30. The following equilibrium pressures were observed at a certain temperature for the reaction

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

$$P_{NH_3} = 3.1 \times 10^{-2} \text{ atm}$$
$$P_{N_2} = 8.5 \times 10^{-1} \text{ atm}$$
$$P_{H_2} = 3.1 \times 10^{-3} \text{ atm}$$

Calculate the value for the equilibrium constant K_p at this temperature.

If $P_{N_2} = 0.525$ atm, $P_{NH_3} = 0.0167$ atm, and $P_{H_2} = 0.00761$ atm, does this represent a system at equilibrium?

31. At 327°C, the equilibrium concentrations are $[CH_3OH] = 0.15$ M, $[CO] = 0.24$ M, and $[H_2] = 1.1$ M for the reaction

$$CH_3OH(g) \rightleftharpoons CO(g) + 2H_2(g)$$

Calculate K_p at this temperature.

32. At 1100 K, $K_p = 0.25$ for the reaction

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

What is the value of K at this temperature?

33. Write expressions for K and K_p for the following reactions.

a. $2NH_3(g) + CO_2(g) \rightleftharpoons N_2CH_4O(s) + H_2O(g)$

b. $2NBr_3(s) \rightleftharpoons N_2(g) + 3Br_2(g)$

c. $2KClO_3(s) \rightleftharpoons 2KCl(s) + 3O_2(g)$

d. $CuO(s) + H_2(g) \rightleftharpoons Cu(l) + H_2O(g)$

34. Write expressions for K_p for the following reactions.

a. $2Fe(s) + \frac{3}{2}O_2(g) \rightleftharpoons Fe_2O_3(s)$

b. $CO_2(g) + MgO(s) \rightleftharpoons MgCO_3(s)$

c. $C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g)$

d. $4KO_2(s) + 2H_2O(g) \rightleftharpoons 4KOH(s) + 3O_2(g)$

35. For which reactions in Exercise 33 is K_p equal to K?

36. For which reactions in Exercise 34 is K_p equal to K?

37. Consider the following reaction at a certain temperature:

$$4Fe(s) + 3O_2(g) \rightleftharpoons 2Fe_2O_3(s)$$

An equilibrium mixture contains 1.0 mole of Fe, 1.0×10^{-3} mole of O_2, and 2.0 moles of Fe_2O_3 all in a 2.0-L container. Calculate the value of K for this reaction.

38. In a study of the reaction

$$3Fe(s) + 4H_2O(g) \rightleftharpoons Fe_3O_4(s) + 4H_2(g)$$

at 1200 K it was observed that when the equilibrium partial pressure of water vapor is 15.0 torr, the total pressure at equilibrium is 36.3 torr. Calculate the value of K_p for this reaction at 1200 K. (*Hint:* Apply Dalton's law of partial pressures.)

Equilibrium Calculations

39. The equilibrium constant is 0.0900 at 25°C for the reaction

$$H_2O(g) + Cl_2O(g) \rightleftharpoons 2HOCl(g)$$

For which of the following sets of conditions is the system at equilibrium? For those that are not at equilibrium, in which direction will the system shift?

a. A 1.0-L flask contains 1.0 mole of HOCl, 0.10 mole of Cl_2O, and 0.10 mole of H_2O.

b. A 2.0-L flask contains 0.084 mole of HOCl, 0.080 mole of Cl_2O, and 0.98 mole of H_2O.

c. A 3.0-L flask contains 0.25 mole of HOCl, 0.0010 mole of Cl_2O, and 0.56 mole of H_2O.

40. The equilibrium constant is 0.0900 at 25°C for the reaction

$$H_2O(g) + Cl_2O(g) \rightleftharpoons 2HOCl(g)$$

For which of the following sets of conditions is the system at equilibrium? For those that are not at equilibrium, in which direction will the system shift?

a. $P_{H_2O} = 1.00$ atm, $P_{Cl_2O} = 1.00$ atm, $P_{HOCl} = 1.00$ atm

b. $P_{H_2O} = 200.$ torr, $P_{Cl_2O} = 49.8$ torr, $P_{HOCl} = 21.0$ torr

c. $P_{H_2O} = 296$ torr, $P_{Cl_2O} = 15.0$ torr, $P_{HOCl} = 20.0$ torr

41. At 900°C, $K_p = 1.04$ for the reaction

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

At a low temperature, dry ice (solid CO_2), calcium oxide, and calcium carbonate are introduced into a 50.0-L reaction chamber. The temperature is raised to 900°C, resulting in the dry ice converting to gaseous CO_2. For the following mixtures, will the initial amount of calcium oxide increase, decrease, or remain the same as the system moves toward equilibrium at 900°C?

a. 655 g $CaCO_3$, 95.0 g CaO, $P_{CO_2} = 2.55$ atm

b. 780 g $CaCO_3$, 1.00 g CaO, $P_{CO_2} = 1.04$ atm

c. 0.14 g $CaCO_3$, 5000 g CaO, $P_{CO_2} = 1.04$ atm

d. 715 g $CaCO_3$, 813 g CaO, $P_{CO_2} = 0.211$ atm

42. Ethyl acetate is synthesized in a nonreacting solvent (not water) according to the following reaction:

$$\underset{\text{Acetic acid}}{CH_3CO_2H} + \underset{\text{Ethanol}}{C_2H_5OH} \rightleftharpoons \underset{\text{Ethyl acetate}}{CH_3CO_2C_2H_5} + H_2O \qquad K = 2.2$$

For the following mixtures (a–d), will the concentration of H_2O increase, decrease, or remain the same as equilibrium is established?

a. $[CH_3CO_2C_2H_5] = 0.22\ M$, $[H_2O] = 0.10\ M$, $[CH_3CO_2H] = 0.010\ M$, $[C_2H_5OH] = 0.010\ M$

b. $[CH_3CO_2C_2H_5] = 0.22\ M$, $[H_2O] = 0.0020\ M$, $[CH_3CO_2H] = 0.0020\ M$, $[C_2H_5OH] = 0.10\ M$

c. $[CH_3CO_2C_2H_5] = 0.88\ M$, $[H_2O] = 0.12\ M$, $[CH_3CO_2H] = 0.044\ M$, $[C_2H_5OH] = 6.0\ M$

d. $[CH_3CO_2C_2H_5] = 4.4\ M$, $[H_2O] = 4.4\ M$, $[CH_3CO_2H] = 0.88\ M$, $[C_2H_5OH] = 10.0\ M$

e. What must the concentration of water be for a mixture with $[CH_3CO_2C_2H_5] = 2.0\ M$, $[CH_3CO_2H] = 0.10\ M$, and $[C_2H_5OH] = 5.0\ M$ to be at equilibrium?

f. Why is water included in the equilibrium expression for this reaction?

43. For the reaction

$$2H_2O(g) \rightleftharpoons 2H_2(g) + O_2(g)$$

$K = 2.4 \times 10^{-3}$ at a given temperature. At equilibrium in a 2.0-L container it is found that $[H_2O(g)] = 1.1 \times 10^{-1}\ M$ and $[H_2(g)] = 1.9 \times 10^{-2}\ M$. Calculate the moles of $O_2(g)$ present under these conditions.

44. The reaction

$$2NO(g) + Br_2(g) \rightleftharpoons 2NOBr(g)$$

has $K_p = 109$ at 25°C. If the equilibrium partial pressure of Br_2 is 0.0159 atm and the equilibrium partial pressure of NOBr is 0.0768 atm, calculate the partial pressure of NO at equilibrium.

45. A 1.00-L flask was filled with 2.00 moles of gaseous SO_2 and 2.00 moles of gaseous NO_2 and heated. After equilibrium was reached, it was found that 1.30 moles of gaseous NO was present. Assume that the reaction

$$SO_2(g) + NO_2(g) \rightleftharpoons SO_3(g) + NO(g)$$

occurs under these conditions. Calculate the value of the equilibrium constant, K, for this reaction.

46. A sample of $S_8(g)$ is placed in an otherwise empty rigid container at 1325 K at an initial pressure of 1.00 atm, where it decomposes to $S_2(g)$ by the reaction

$$S_8(g) \rightleftharpoons 4S_2(g)$$

At equilibrium, the partial pressure of S_8 is 0.25 atm. Calculate K_p for this reaction at 1325 K.

47. At a particular temperature, 12.0 moles of SO_3 is placed into a 3.0-L rigid container, and the SO_3 dissociates by the reaction

$$2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$$

At equilibrium, 3.0 moles of SO_2 is present. Calculate K for this reaction.

48. At a particular temperature, 8.0 moles of NO_2 is placed into a 1.0-L container and the NO_2 dissociates by the reaction

$$2NO_2(g) \rightleftharpoons 2NO(g) + O_2(g)$$

At equilibrium the concentration of NO(g) is 2.0 M. Calculate K for this reaction.

49. An initial mixture of nitrogen gas and hydrogen gas is reacted in a rigid container at a certain temperature by the reaction

$$3H_2(g) + N_2(g) \rightleftharpoons 2NH_3(g)$$

At equilibrium, the concentrations are $[H_2] = 5.0\ M$, $[N_2] = 8.0\ M$, and $[NH_3] = 4.0\ M$. What were the concentrations of nitrogen gas and hydrogen gas that were reacted initially?

50. Nitrogen gas (N_2) reacts with hydrogen gas (H_2) to form ammonia (NH_3). At 200°C in a closed container, 1.00 atm of nitrogen gas is mixed with 2.00 atm of hydrogen gas. At equilibrium, the total pressure is 2.00 atm. Calculate the partial pressure of hydrogen gas at equilibrium, and calculate the K_p value for this reaction.

51. At a particular temperature, $K = 3.75$ for the reaction

$$SO_2(g) + NO_2(g) \rightleftharpoons SO_3(g) + NO(g)$$

If all four gases had initial concentrations of 0.800 *M*, calculate the equilibrium concentrations of the gases.

52. At a particular temperature, $K = 1.00 \times 10^2$ for the reaction

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

In an experiment, 1.00 mole of H_2, 1.00 mole of I_2, and 1.00 mole of HI are introduced into a 1.00-L container. Calculate the concentrations of all species when equilibrium is reached.

53. At 2200°C, $K_p = 0.050$ for the reaction

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$$

What is the partial pressure of NO in equilibrium with N_2 and O_2 that were placed in a flask at initial pressures of 0.80 and 0.20 atm, respectively?

54. At 25°C, $K = 0.090$ for the reaction

$$H_2O(g) + Cl_2O(g) \rightleftharpoons 2HOCl(g)$$

Calculate the concentrations of all species at equilibrium for each of the following cases.

a. 1.0 g H_2O and 2.0 g Cl_2O are mixed in a 1.0-L flask.

b. 1.0 mole of pure HOCl is placed in a 2.0-L flask.

55. At 1100 K, $K_p = 0.25$ for the reaction

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

Calculate the equilibrium partial pressures of SO_2, O_2, and SO_3 produced from an initial mixture in which $P_{SO_2} = P_{O_2} = 0.50$ atm and $P_{SO_3} = 0$. (*Hint:* If you don't have a graphing calculator, then use the method of successive approximations to solve, as discussed in Appendix 1.4.)

56. At a particular temperature, $K_p = 0.25$ for the reaction

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

a. A flask containing only N_2O_4 at an initial pressure of 4.5 atm is allowed to reach equilibrium. Calculate the equilibrium partial pressures of the gases.

b. A flask containing only NO_2 at an initial pressure of 9.0 atm is allowed to reach equilibrium. Calculate the equilibrium partial pressures of the gases.

c. From your answers to parts a and b, does it matter from which direction an equilibrium position is reached?

57. At 35°C, $K = 1.6 \times 10^{-5}$ for the reaction

$$2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g)$$

Calculate the concentrations of all species at equilibrium for each of the following original mixtures.

a. 2.0 moles of pure NOCl in a 2.0-L flask

b. 1.0 mole of NOCl and 1.0 mole of NO in a 1.0-L flask

c. 2.0 moles of NOCl and 1.0 mole of Cl_2 in a 1.0-L flask

58. At a particular temperature, $K = 4.0 \times 10^{-7}$ for the reaction

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

In an experiment, 1.0 mole of N_2O_4 is placed in a 10.0-L vessel. Calculate the concentrations of N_2O_4 and NO_2 when this reaction reaches equilibrium.

59. At a particular temperature, $K = 2.0 \times 10^{-6}$ for the reaction

$$2CO_2(g) \rightleftharpoons 2CO(g) + O_2(g)$$

If 2.0 moles of CO_2 is initially placed into a 5.0-L vessel, calculate the equilibrium concentrations of all species.

60. Lexan is a plastic used to make compact discs, eyeglass lenses, and bullet-proof glass. One of the compounds used to make Lexan is phosgene ($COCl_2$), an extremely poisonous gas. Phosgene decomposes by the reaction

$$COCl_2(g) \rightleftharpoons CO(g) + Cl_2(g)$$

for which $K_p = 6.8 \times 10^{-9}$ at 100°C. If pure phosgene at an initial pressure of 1.0 atm decomposes, calculate the equilibrium pressures of all species.

61. At 25°C, $K_p = 2.9 \times 10^{-3}$ for the reaction

$$NH_4OCONH_2(s) \rightleftharpoons 2NH_3(g) + CO_2(g)$$

In an experiment carried out at 25°C, a certain amount of NH_4OCONH_2 is placed in an evacuated rigid container and allowed to come to equilibrium. Calculate the total pressure in the container at equilibrium.

62. A sample of solid ammonium chloride was placed in an evacuated container and then heated so that it decomposed to ammonia gas and hydrogen chloride gas. After heating, the total pressure in the container was found to be 4.4 atm. Calculate K_p at this temperature for the decomposition reaction

$$NH_4Cl(s) \rightleftharpoons NH_3(g) + HCl(g)$$

Le Châtelier's Principle

63. Suppose the reaction system

$$UO_2(s) + 4HF(g) \rightleftharpoons UF_4(g) + 2H_2O(g)$$

has already reached equilibrium. Predict the effect that each of the following changes will have on the equilibrium position. Tell whether the equilibrium will shift to the right, will shift to the left, or will not be affected.

a. Additional $UO_2(s)$ is added to the system.

b. The reaction is performed in a glass reaction vessel; $HF(g)$ attacks and reacts with glass.

c. Water vapor is removed.

64. Predict the shift in the equilibrium position that will occur for each of the following reactions when the volume of the reaction container is increased.

a. $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

b. $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

c. $H_2(g) + F_2(g) \rightleftharpoons 2HF(g)$

d. $COCl_2(g) \rightleftharpoons CO(g) + Cl_2(g)$

e. $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$