Chemistry

Chapter 13
Chemical Equilibrium

Section 2

Chapters:

13.5 Applications of the equilibrium constant

13.6 Solving equilibrium problems

13.7 La Chatlier’s principle

What can we use the equilibrium constant for?

- Helps in predicting features of reactions, which includes determining:
  - Tendency (not speed) of a reaction to occur
  - Whether a given set of concentrations represents an equilibrium condition
  - Equilibrium position that will be achieved from a given set of initial concentrations

Applications of chemical equilibrium

- In most scenarios we actually only know the initial concentrations of our reaction

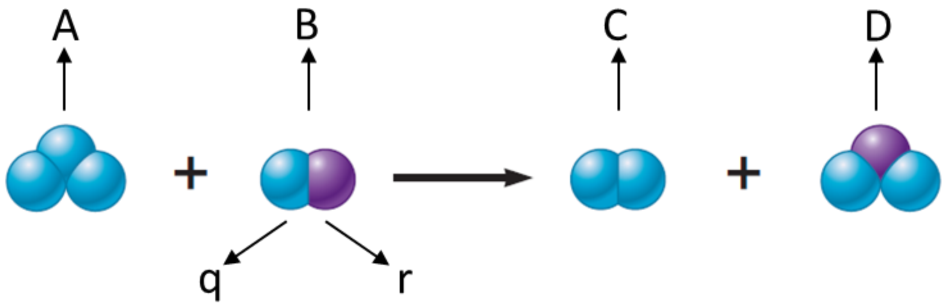
- K is also known for most reactions at a given temperature.

https://www.nist.gov/srd

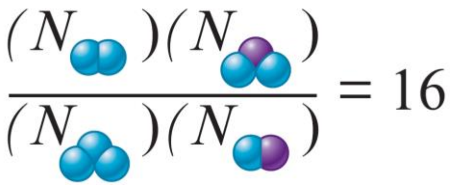
- There is a ton of data on reactions that we can use to predict the equilibrium concentrations of species

Applications of chemical equilibrium

- Consider the following reaction:

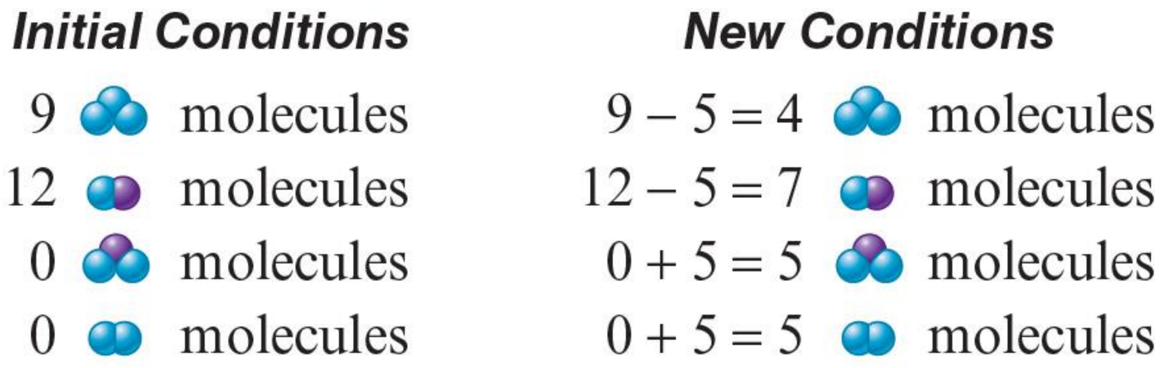


  - q and r represent two different types of atoms
  - Assume that the equilibrium constant is 16



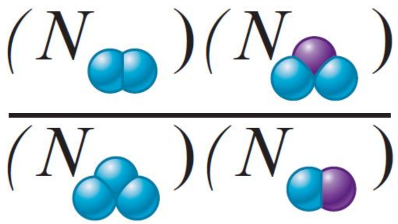
Applications of chemical equilibrium

- Assume that five molecules of A disappear so that the system can reach equilibrium
  - To maintain equilibrium, 5 molecules of B will also disappear, forming 5 C and 5 D molecules



Applications of chemical equilibrium

- The new conditions do not match the equilibrium position

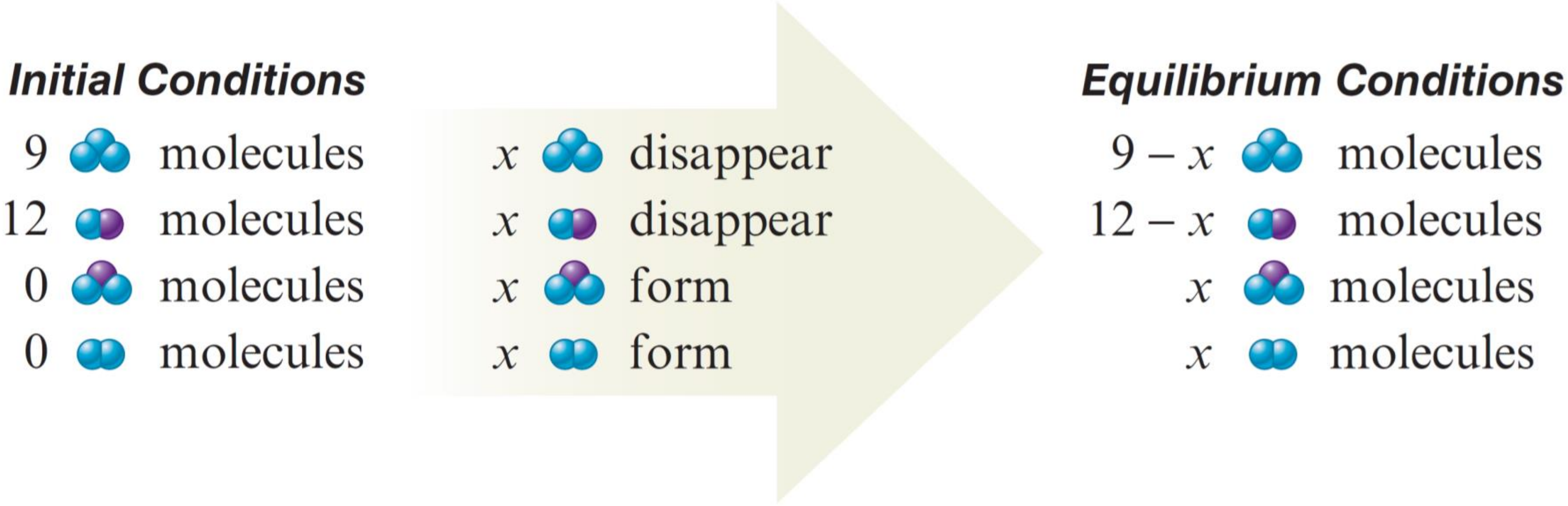


$$= \frac{(5)(5)}{(4)(7)} = 0.9$$

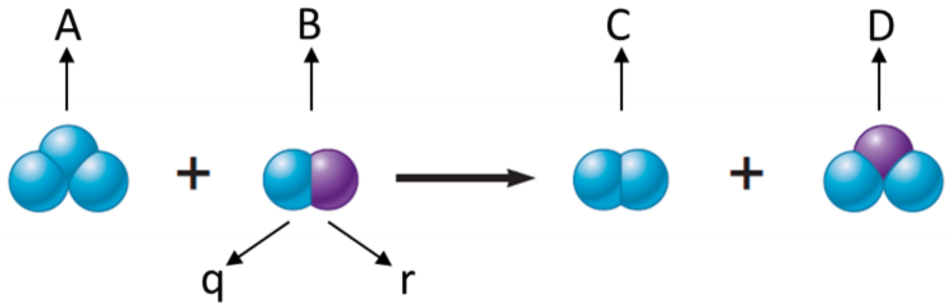
  - Equilibrium can be achieved by increasing the numerator and decreasing the denominator
    - System moves to the right - More than 5 original reactant molecules disappear

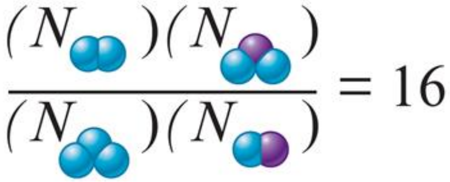
Applications of chemical equilibrium

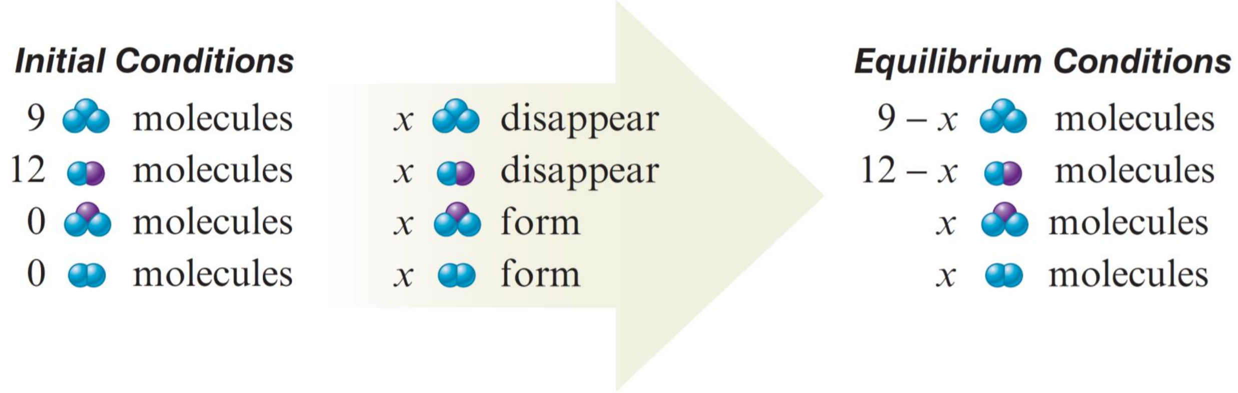
- Let *x* be the number of molecules that need to disappear so that the system can reach equilibrium

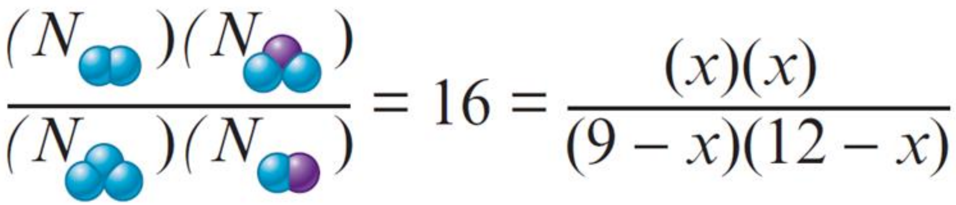


Applications of chemical equilibrium









Applications of chemical equilibrium

- So obviously we are gunna have to do some serious algebra. I’m going to teach you a fail proof method on how to set up these problems, I will solve some problems and go through the algebra but at this point it is up to you to know the algebra. I can’t spend most of the time teaching algebraic manipulation.

Applications of chemical equilibrium

We are going to learn the all powerful rice table.

R - Reaction

I - Initial

C - Change

E - Equilibrium

Knowing how to build these and use them to solve chemical equilibrium problems can carry you a long way in college chemistry and even further into your chemistry career.

Applications of chemical equilibrium

Let's say I have a reaction

$$\boldsymbol{A(g) + B(g) \rightarrow C(g) + D(g)}$$

For this scenario let's say we are given K = 1.2×10^{-2} and our initial concentrations are [A] = .5 M, [B] = .4 M, [C] = 0M and [D] = 0M and we need to find the equilibrium concentrations.

Applications of chemical equilibrium

Build the RICE TABLE!

R	$\boldsymbol{A(g)+B(g)\ \rightarrow C(g)+D(g)}$			
I	.5 M	.4 M	0 M	0 M
C	-x	-x	+x	+x
E	.5 M -x	.4M-x	x	x

$$K=\frac{[x]\,[x]}{[.5\ -x]\,[.4\ -x]}$$

Applications of chemical equilibrium

And now comes the algebra

$$K = \frac{[x]\,[x]}{[.5\ - x]\,[.4\ - x]} \qquad K = 1.2\ *\ 10^{-2}$$

1 $1.2\ *\ 10^{-2} = \frac{[x]\,[x]}{[.5\ -x]\,[.4\ -x]} \ \rightarrow\ 1.2\ * 10^{-2}\,(.5 - x)(.4 - x) =\ x^2$

2 $1.2\ * 10^{-2}\,(.5 - x)(.4 - x) =\ x^2\ \rightarrow 1.2\ * 10^{-2}\,(.20\ -\ .9x + x^2) =\ x^2$

3 $1.2\ * 10^{-2}\,(.20\ -\ .9x + x^2) =\ x^2 \rightarrow\ 2.4\ *\ 10^{-3}\ - .0108x + 1.2\ *\ 10^{-2}x^2 =\ x^2$

4 $2.4\ *\ 10^{-3}\ - .0108x + 1.2\ *\ 10^{-2}x^2 =\ x^2\ \rightarrow \mathbf{2.4\ *\ 10^{-3} - .0108x - .988x^2 = 0}$

Applications of chemical equilibrium

We want to make that whole mess equal zero

$$\mathbf{2.4 * 10^{-4} - .0108x - .988x^2 = 0}$$

Now we can use the quadratic formula.

a b c

$$\mathbf{-.988x^2 - .0108x + 2.4 * 10^{-3} = 0}$$

We always want the positive answer

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{.0108 \pm \sqrt{.0108^2 - (4 * -.988 * 2.4 * 10^{-3})}}{2(-.988)} = \frac{.0108 \pm .0979}{-1.976}$$

$$\boldsymbol{x = .044\ M}$$

Applications of chemical equilibrium

Now we have x so lets solve for our equilibrium concentrations

$$x = .110\ M$$

R	$A(g)$	$+\ B(g)$	$\rightarrow C(g)$	$+\ D(g)$
I	.5 M	.4 M	0 M	0 M
C	-x	-x	+x	+x
E	.5 M -x	.4M-x	x	x

Final Answer:

[A(g)] = .5 - .044 = .456M

[B(g)] = .4 - .044 = .356 M

[C(g)] = 0 + .044 = .044 M

[D(g)] = 0 + .044 = .044 M

Applications of chemical equilibrium

Something to note to make our lives easier.

Let's say K is extremely small compared to our initial concentrations meaning $K < 10^{-4}$ factors of 10 smaller than our initial concentrations.

$$K = 1.2 \times 10^{-5}$$

We can assume that the initial concentration minus x is negligible

$$K = \frac{[x]\,[x]}{[.5\ - x]\,[.4\ - x]} \approx \frac{[x^2]}{[.5][.4]}$$

Which is way easier to solve than the quadratic

Applications of chemical equilibrium

What happens if it is not a 1:1 molar ratio though?

Applications of chemical equilibrium

Lets go back to our general problem but with coefficients

$$2A(g) + 3B(g) \rightarrow 4C(g) + D(g)$$

We are still going to build our rice table but we need to take into account our molar ratios.

Applications of chemical equilibrium

R	$2A(g)$	$+ 3B(g)$	$\rightarrow 4C(g)$	$+ D(g)$
I	.5 M	.4 M	0 M	0 M
C	-x	$-\frac{3}{2}$x	+ 2x	+ $\frac{1}{2}$x
E	.5 - x M	.4 - $\frac{3}{2}$x M	2x M	$\frac{1}{2}$x M

$$K = \frac{[2x]^4 \left[\frac{1}{2}\, x\right]}{[.5 - x]^2 \left[.4 - \frac{3}{2} x\right]^3}$$

Applications of chemical equilibrium

Will I ever ask you to solve an expression like this?

$$K = \frac{[2x]^4 \left[\frac{1}{2}\, x\right]}{[.5\ - x]^2 \left[.4\ - \frac{3}{2} x\right]^3}$$

No, that is absurd and that is why we have computers. However, I will ask you to build me an expression to find the equilibrium constants for a reaction with varying coefficients.

Applications of chemical equilibrium

So what is this actually telling us?

R	$2A(g) +$	$3B(g)$	$\rightarrow 4C(g) +$	$D(g)$
I	.5 M	.4 M	0 M	0 M
C	-x	$-\frac{3}{2}$x	+ 2x	+ $\frac{1}{2}$x
E	.5 - x M	.4 - $\frac{3}{2}$x M	2x M	$\frac{1}{2}$x M

This is telling us that for every 2 mols of A that react 3 mols of B must react. For every 2 mols of A and 3 mols of B that react I generate 4 mols of C and 1 mol of D

Applications of chemical equilibrium

An easy way to figure out the coefficient on x

$$\mathbf{2}\boldsymbol{A}(\boldsymbol{g}) + \mathbf{3}\boldsymbol{B}(\boldsymbol{g}) \rightarrow \mathbf{4}\boldsymbol{C}(\boldsymbol{g}) + \boldsymbol{D}(\boldsymbol{g})$$

If I pick [A] to host my x I will divide all my coefficients by A's coefficient to determine the coefficient on x for each part.

Applications of chemical equilibrium

What happens when I'm given initial concentrations for all species?

Applications of chemical equilibrium

$$A(g) + B(g) \rightarrow C(g) + D(g)$$

For this scenario let's say we are given K = 1.2×10^{-2} and our initial concentrations are [A] = .5 M, [B] = .4 M, [C] = .2M and [D] = .3M and we need to find the equilibrium concentrations.

How do we know which way the reaction will run?

Applications of chemical equilibrium

For these problems we need to use the reaction quotient Q

We solve for Q the exact same way we solve for K except we use **initial** concentrations.

So Q is for initial **K is for equilibrium**

Applications of chemical equilibrium

Back to our original problem

$$\boldsymbol{A(g) + B(g) \rightarrow C(g) + D(g)}$$

Initial = [A] = .5 M, [B] = .4 M, [C] = .2M, [D] = .3M

$$Q = \frac{[.2][.3]}{[.5][.4]} = .3$$

Applications of chemical equilibrium

We then compare Q to our given K value.

$$Q = \frac{[.2][.3]}{[.5][.4]} = .3$$

K = 1.2 x 10^{-2}

- If Q > K or Q is bigger than K then the reaction will run towards the reactants.
- If Q < K or Q is less than K then the reaction will run towards the products.

Applications of chemical equilibrium

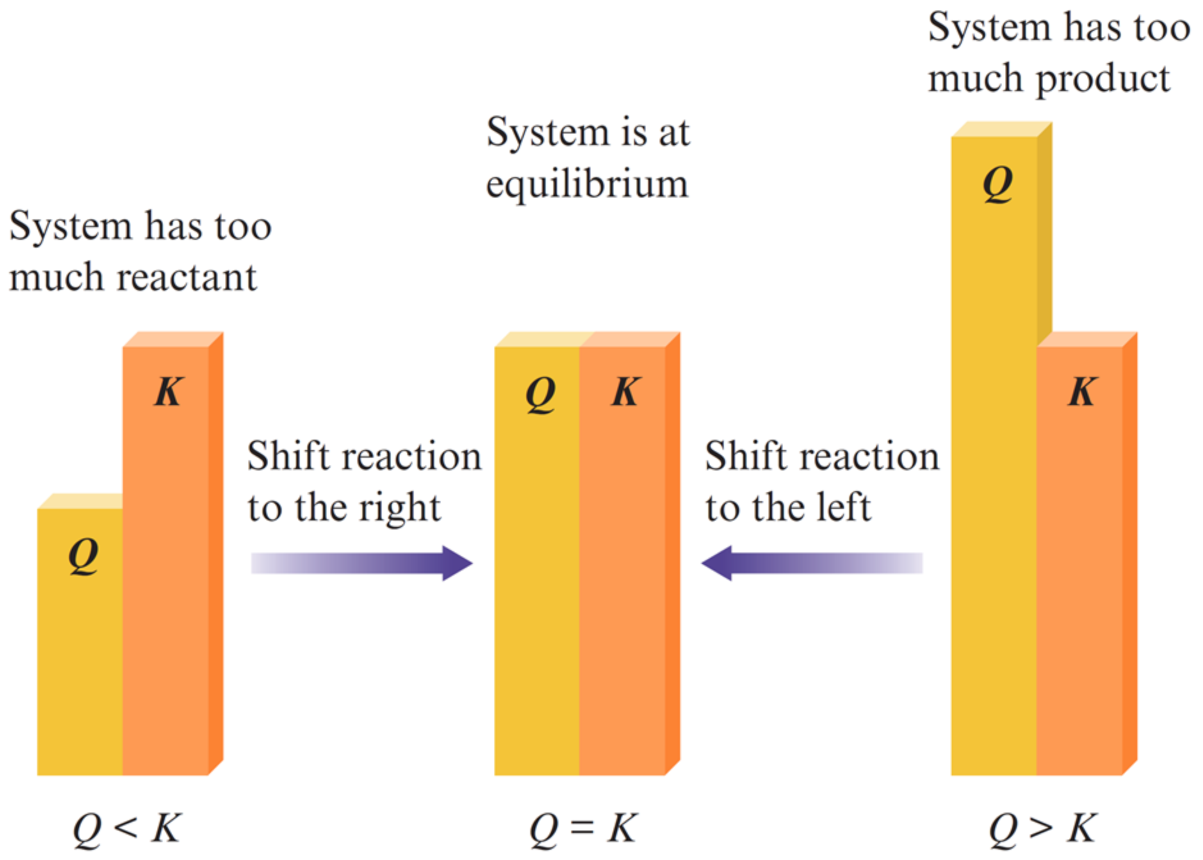
In this scenario Q is bigger than K so our RICE table will look like this

$$Q = \frac{[.2][.3]}{[.5][.4]} = .3 \qquad K = 1.2 \times 10^{-2}$$

R	$\boldsymbol{A}(\boldsymbol{g}) +$	$\boldsymbol{B}(\boldsymbol{g}) \rightarrow$	$\boldsymbol{C}(\boldsymbol{g}) +$	$\boldsymbol{D}(\boldsymbol{g})$
I	.5 M	.4 M	.2 M	.3 M
C	+x	+x	-x	-x
E	.5 M +x	.4M+x	.2 -x	.3 - x

$$K = \frac{[.2 - x]\,[.3 - x]}{[.5 + x]\,[.4 + x]}$$

Applications of chemical equilibrium



Applications of chemical equilibrium

- For the synthesis of ammonia at 500° C, the equilibrium constant is 6.0×10^{-2}
  - Predict the direction in which the system will shift to reach equilibrium in the following case:
    - $[NH_3]_0 = 1.0 \times 10^{-3}\ M$
    - $[N_2]_0 = 1.0 \times 10^{-5}\ M$
    - $[H_2]_0 = 2.0 \times 10^{-3}\ M$

$$3H_2 + N_2 \leftrightarrow 2NH_3$$

Applications of chemical equilibrium

- Typical equilibrium problem
  - Determine equilibrium concentrations of reactants and products
    - Value of equilibrium constant and initial concentrations are provided
- Mathematically complicated problem
  - Develop strategies to solve the problem using the information provided

Applications of chemical equilibrium

- Consider an experiment in which gaseous N_2O_4 was placed in a flask and allowed to reach equilibrium at a temperature where K_p = 0.133
  - At equilibrium, the pressure of N_2O_4 was found to be 2.71 atm
  - Calculate the equilibrium pressure of $NO_2(g)$

$$N_2O_4(g) \rightarrow 2NO_2(\mathrm{g})$$

Applications of chemical equilibrium

- At a certain temperature, a 1.00-L flask initially contained 0.298 mole of PCl_3(*g*) and 8.70×10^{-3} mole of PCl_5 (*g*)
  - After the system had reached equilibrium, 2.00×10^{-3} mole of Cl_2 (*g*) was found in the flask
  - Gaseous PCl_5 decomposes according to the reaction

$$PCl_5(g) \leftrightarrow PCl_3(g) + Cl_2(g)$$

    - Calculate the equilibrium concentrations of all species and the value of *K*

Applications of chemical equilibrium

- Assume that the reaction for the formation of gaseous hydrogen fluoride from hydrogen and fluorine has an equilibrium constant of 1.15×10^2 at a certain temperature
  - In a particular experiment, 3.000 moles of each component were added to a 1.500-L flask
  - Calculate the equilibrium concentrations of all species

Applications of chemical equilibrium

- Assume that the reaction for the formation of gaseous hydrogen fluoride from hydrogen and fluorine has an equilibrium constant of 1.15×10^2 at a certain temperature
  - In a particular experiment, 3.000 moles of each component were added to a 1.500-L flask
  - Calculate the equilibrium concentrations of all species

Here is the strategy for solving equilibrium problems in words

1. Write the balanced equation for the reaction
2. Calculate Q to determine which way the reaction will run when given a K
3. Build the RICE table!
4. Do the maths… (Solve for the unknown)
5. Use the unknown to find equilibrium concentrations

More Practice

- Assume that gaseous hydrogen iodide is synthesized from hydrogen gas and iodine vapor at a temperature where the equilibrium constant is 1.00×10^{2}
  - Suppose HI at 5.000×10^{-1} atm, H_2 at 1.000×10^{-2} atm, and I_2 at 5.000×10^{-3} atm are mixed in a 5.000-L flask
    - Calculate the equilibrium pressures of all species

More Practice

- Assume that gaseous hydrogen iodide is synthesized from hydrogen gas and iodine vapor at a temperature where the equilibrium constant is 1.00×10^2
  - Suppose HI at 5.000×10^{-1} atm, H_2 at 1.000×10^{-2} atm, and I_2 at 5.000×10^{-3} atm are mixed in a 5.000-L flask
    - Calculate the equilibrium pressures of all species

More Practice

- Consider the decomposition of gaseous NOCl at 35° C with an equilibrium constant of 1.6×10^{-5}
  - The following steps determine the equilibrium concentrations of NOCl, NO, and Cl_2 when one mole of NOCl is placed in a 2.0-L flask:
  - The balanced equation is

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

Find the equilibrium concentrations

Le Chatelier's Principle

- If a change is imposed on a system at equilibrium, the position of the equilibrium will shift in a direction that tends to reduce that change
- Helps in the qualitative prediction of the effects of changes in concentration, pressure, and temperature on a system at equilibrium

Le Chatelier's Principle

- If a component is added to a reaction system at equilibrium, the equilibrium position will shift in the direction that lowers the concentration of that component
  - If a component is removed, the opposite effect occurs
    - System at equilibrium exists at constant *T* and *P* or constant *T* and *V*

Le Chatelier's Principle

- Arsenic can be extracted from its ores by first reacting the ore with oxygen (called roasting) to form solid As_4O_6, which is then reduced using carbon

$$As_4O_6\,(s) + 6C(s) \rightarrow As_4(g) + 6CO(g)$$

Le Chatelier's Principle

- Predict the direction of the shift of the equilibrium position in response to each of the following changes in conditions:
  a. Addition of carbon monoxide
  b. Addition or removal of carbon or tetraarsenic hexoxide (As_4O_6)
  c. Removal of gaseous arsenic (As_4)

$$As_4O_6\,(s) + 6C(s) \rightarrow As_4(g) + 6CO(g)$$

Le Chatelier's Principle

a. Le Châtelier's principle predicts that the shift will be away from the substance whose concentration is increased
   - Equilibrium position will shift to the left when carbon monoxide is added

b. The amount of a pure solid has no effect on the equilibrium position

Le Chatelier's Principle

- Changing the amount of carbon or tetraarsenic hexoxide will have no effect

c. If gaseous arsenic is removed, the equilibrium position will shift to the right to form more products

- In industrial processes, the desired product is often continuously removed from the reaction system to increase the yield

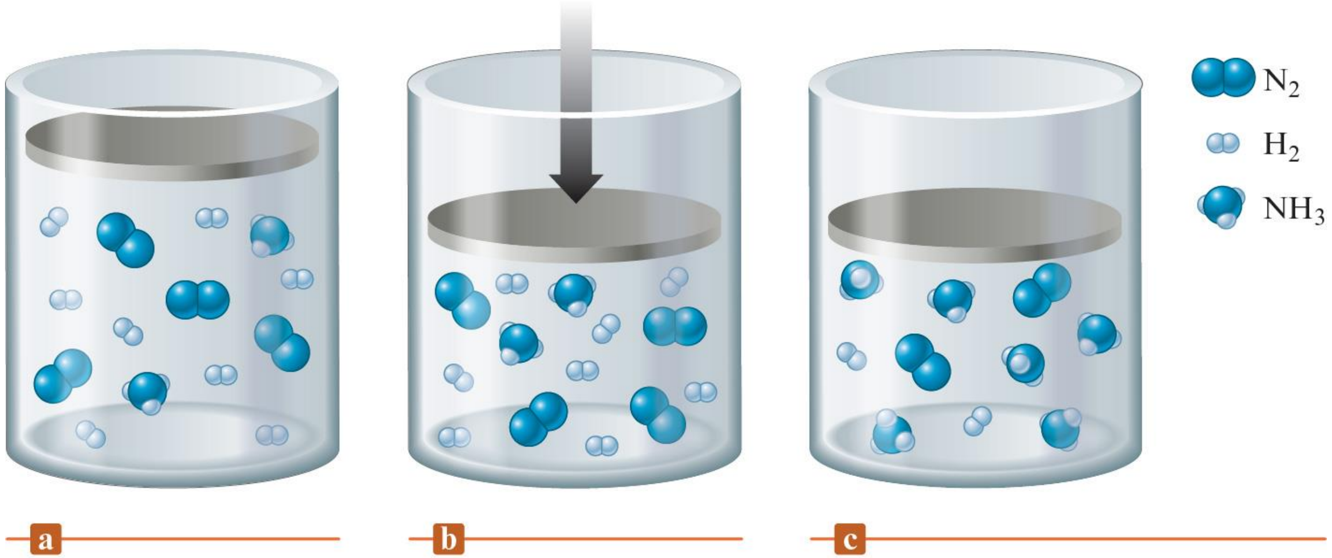
Le Chatelier's Principle

- Methods used to change the pressure of a reaction system with gaseous components:
  - Add or remove a gaseous reactant or product
  - Add an inert gas (not the one involved in the reaction)
  - Change the volume of the container

Le Chatelier’s Principle

- Addition of an inert gas increases the total pressure
  - Does not affect the concentrations or partial pressures of the reactants or products
- When the volume of the container holding a gaseous system is reduced, the system responds by reducing its own volume
  - Total number of gaseous molecules is reduced

Le Chatelier's Principle



(a) A mixture of NH_3(g), N_2(g), and H_2(g) at equilibrium
(b) The volume is suddenly decreased
(c) The new equilibrium position for the system containing more NH_3 and less N_2 and H_2

Le Chatelier's Principle

- Predict the shift in equilibrium position that will occur during the preparation of liquid phosphorus trichloride

$$P_4(s) + 6Cl_2\,(g) \;\leftrightarrow 4PCl_3(l)$$

  - Assume that the volume is reduced

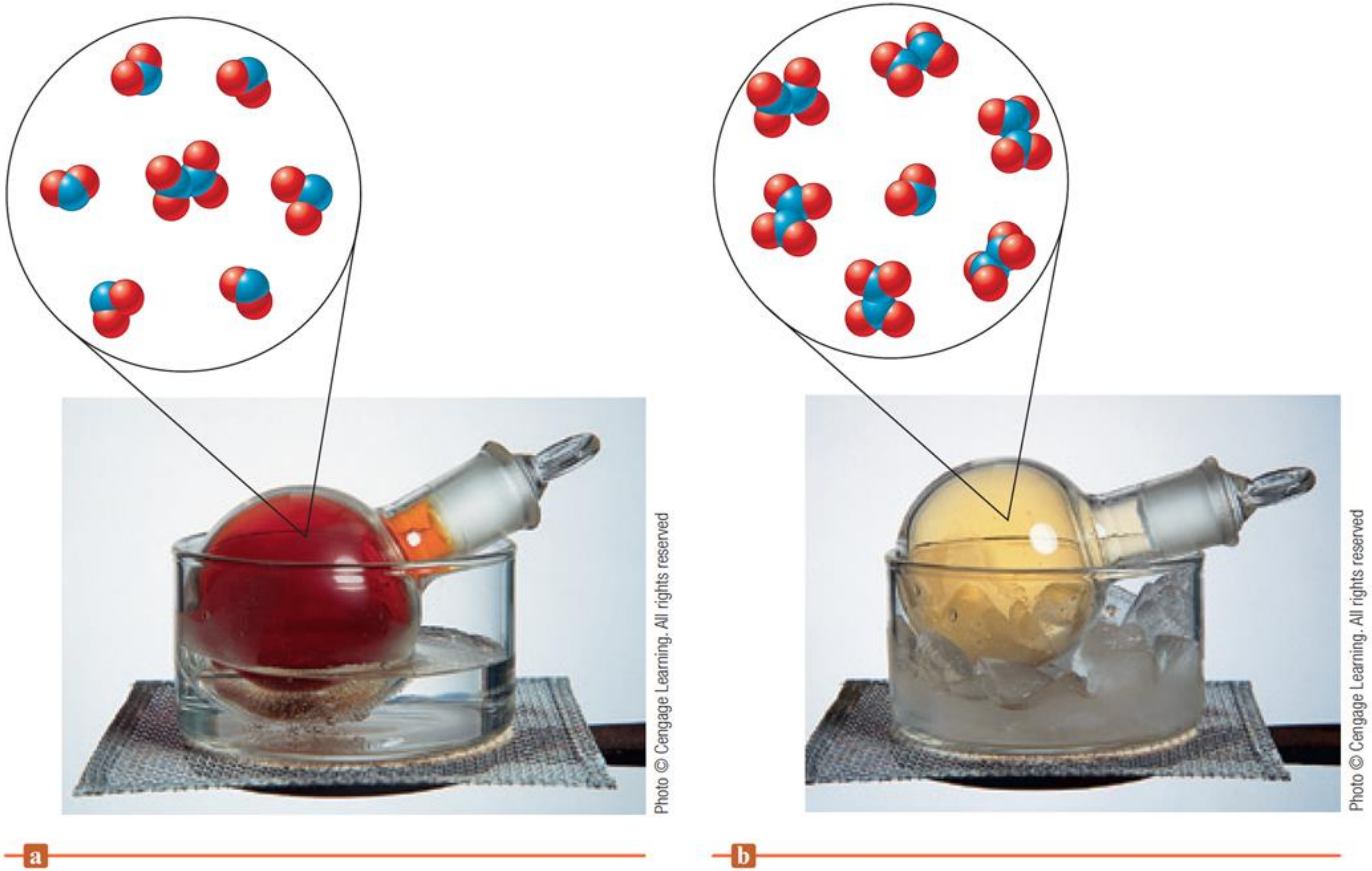
Le Chatelier's Principle

- Value of *K* changes with the temperature
- Consider the synthesis of ammonia, an exothermic reaction

$$N_2 + 3H_2 \rightarrow 2NH_3 + 92\ kJ$$

  - According to Le Châtelier's principle, the shift will be in the direction that consumes energy
    - Concentration of NH_3 decreases and that of N_2 and H_2 increases, thus decreasing the value of *K*

Le Chatelier’s Principle




SUPERB wallpapers
That's all Folks!

Chemistry

Chapter 13
Chemical Equilibrium

Section 2

HW: Pg 547b – 547h

Problems: 55 – 129 Not Collected

Do as many as you feel like you need to in order to be successful for this section