

ALE 6. Reversible Reactions(Reference: 17.1 – 17.2 Silberberg 5th edition)**How are equilibrium concentrations of reactants and products related?****Exercise**

Split your team into two groups for this exercise—half of you will be the “Reactants” and you will start off with 100 pennies. The other half of you will be the “Products” and you will start off with 0 pennies. With each passage of time, **t**, the **Reactants** will *set to the side one-third* of the number of pennies they currently have, The **Products** will *set to the side one-fourth* of the number of pennies they currently have, and *then both groups will pass to the other the pennies they’ve set aside and count the new number of pennies they now have*. If you are to set to the side a fraction of a penny, do so only if the fraction is greater than half a penny. (The total number of pennies *cannot* deviate from 100.) Record in the table how many pennies the “Reactants” and the “Products” have after each passage of time.

time	# of Pennies held by reactants	# of Pennies held by products
0	100	0
t		
2t		
3t		
4t		
5t		
6t		
7t		
8t		

Key Questions

- When the numbers of pennies held by each group in the exercise no longer changed, we say that the system has “reached **equilibrium**”. Is this a **dynamic** equilibrium or a **static** equilibrium? Explain your answer using specific numerical data from the coin simulation.
- We’ll think of the “rate constant of the forward reaction” (k_f) to be equal to the fraction of pennies the Reactants passed to the Products, and the “rate of the reverse reaction” (k_r) is equal to the fraction of pennies the Products passed to The Reactants. What are the numerical values of k_f , of k_r , and of k_f/k_r ?
 $k_f =$ _____ $k_r =$ _____ $\frac{k_f}{k_r} =$ _____
- What is the numerical value (rounded to three significant figures) of the ratio of pennies held by the Products to pennies held by the Reactants when the system reached equilibrium? This value should be familiar. What other quantity encountered today is essentially equal to the equilibrium ratio of pennies held by The Products to pennies held by The Reactants?

4. Consider the following generic reversible reaction: $2 A \rightleftharpoons B + C$

To emphasize that the forward reaction occurs through the bimolecular collision of two A molecules the equation may be written as: $A + A \rightleftharpoons B + C$.

The reverse reaction occurs through the bimolecular collision of a B molecule with a C molecule.

a. Finish the rate law for the forward reaction. $\text{Rate}_{\text{fwd}} =$

b. Finish the rate law for the reverse reaction. $\text{Rate}_{\text{rev}} =$

c. At equilibrium, the rate of the reverse reaction becomes equal to the rate of the forward reaction. Set the rate expressions (involving rate constants and molar concentrations of reactants and products) in Questions 4a and 4b equal to each other.

d. Rearrange the equation in Question 4c to solve for k_f/k_r .

e. How did the stoichiometric coefficient of the reactant A get incorporated into the expression for k_f/k_r ?

5 a. The forward rate *constant* divided by the reverse rate *constant* is just another _____.
(Fill in the blank with the correct word.)

b. Let's test that assumption. Let's consider the reversible reaction between sulfur dioxide and oxygen to yield sulfur trioxide at 1500 K.

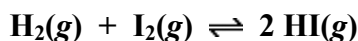


In Experiment 1, SO_2 and O_2 were injected into a reaction vessel having initial concentrations of 0.400 M and 0.200 M, respectively. In Experiment II, pure SO_3 started in the reaction vessel with an initial concentration of 0.500 M. The following table reports the equilibrium concentrations for the two experiments. Complete the table. (SO_3 concentration determines the # of sig figs.)

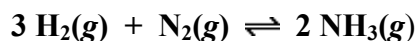
Expmt	$[\text{SO}_2]_{\text{eq}}$	$[\text{O}_2]_{\text{eq}}$	$[\text{SO}_3]_{\text{eq}}$	$\frac{[\text{SO}_3]_{\text{eq}}}{[\text{SO}_2]_{\text{eq}}[\text{O}_2]_{\text{eq}}}$	$\frac{[\text{SO}_3]_{\text{eq}}^2}{[\text{SO}_2]_{\text{eq}}^2[\text{O}_2]_{\text{eq}}}$
1	0.344	0.172	0.056		
2	0.424	0.212	0.076		

c. Why must $[\text{SO}_3]_{\text{eq}}$ and $[\text{SO}_2]_{\text{eq}}$ be squared before a ratio of the concentrations of products to the concentrations of reactants is evaluated?

6. Let's see how "universal" such use of stoichiometric coefficients is. The reaction between hydrogen and iodine gases to produce hydrogen iodide at 425.4 °C



and the reaction between hydrogen and nitrogen gases to produce ammonia at 500 °C



were both studied. The equilibrium concentrations from two experiments of each reaction are tabulated below. Calculate the values in the last two columns in each table.

a.

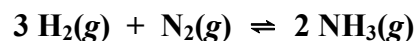
Experiment	$[\text{H}_2]_{\text{eq}}$	$[\text{I}_2]_{\text{eq}}$	$[\text{HI}]_{\text{eq}}$	$\frac{[\text{HI}]_{\text{eq}}}{[\text{H}_2]_{\text{eq}} [\text{I}_2]_{\text{eq}}}$	$\frac{[\text{HI}]_{\text{eq}}^2}{[\text{H}_2]_{\text{eq}} [\text{I}_2]_{\text{eq}}}$
1	0.0018	0.0031	0.0177		
2	0.0011	0.0011	0.0084		

b.

Experiment	$[\text{H}_2]_{\text{eq}}$	$[\text{N}_2]_{\text{eq}}$	$[\text{NH}_3]_{\text{eq}}$	$\frac{[\text{NH}_3]_{\text{eq}}}{[\text{H}_2]_{\text{eq}} [\text{N}_2]_{\text{eq}}}$	$\frac{[\text{NH}_3]_{\text{eq}}^2}{[\text{H}_2]_{\text{eq}}^3 [\text{N}_2]_{\text{eq}}}$
1	0.500	1.00	0.0866		
2	1.35	1.15	0.412		

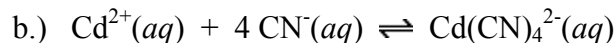
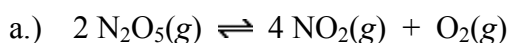
Exercise

7. The ratio k_f/k_r is a constant and is written as K , the **equilibrium constant**. We've just seen that the production of ammonia has the chemical equation and the accompanying **law of mass action** shown to the right. ("Law" = "equation".)



$$K_c = \frac{[\text{NH}_3]_{\text{eq}}^2}{[\text{H}_2]_{\text{eq}}^3 [\text{N}_2]_{\text{eq}}}$$

Write the law of mass action for the following reactions:



Model: Reaction Quotient

When reactants (and/or perhaps products too) are mixed together, the resulting reaction mixture is very likely not to involve equilibrium concentrations. Once mixed, it's possible that the concentrations of the reactants will decrease while the reaction proceeds and the concentrations of the products will increase. Eventually the concentrations of reactants and products reach their equilibrium levels. At this point the forward reaction rate and reverse reaction rates become equal so that no net reaction is taking place.

Consider the generic reversible one-phase reaction in equation 1:



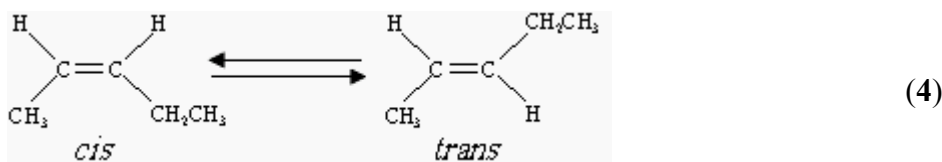
When reactant and product concentrations are equilibrium concentrations, they are related to the reaction's equilibrium constant (K_c) through a **law of mass action** (eqn 2). But when reactant and product concentrations are *not* equilibrium concentrations, they are related to the reaction's **reaction quotient** (Q) through a similar law of mass action (eq 1b).

$$K_c = \frac{[D]_{eq}^d [E]_{eq}^e}{[A]_{eq}^a [B]_{eq}^b} \quad (2)$$

$$Q_c = \frac{[D]^d [E]^e}{[A]^a [B]^b} \quad (3)$$

Key Questions

8. Consider the gaseous isomerization of *cis*-2-pentene to *trans*-2-pentene (eqn 4) at 400 K:



- Write the law of mass action that would be used to evaluate the reaction quotient. (Use the abbreviations “cis” for *cis*-2-pentene and “trans” for *trans*-2-pentene.)
- Calculate the reaction quotient, Q_c , if at some moment in time, in a 10.0-L reaction vessel at 400 K, a reaction mixture contains 0.15 mol of *cis*-2-pentene and 0.15 mol of *trans*-2-pentene.
- If the equilibrium constant (K_c) is 3.0 at 400 K, how does the reaction quotient compare to the equilibrium constant? (Circle your choice.)
 - $Q < K$
 - $Q = K$
 - $Q > K$
- In order for the system to reach a state of equilibrium, which of the following must take place. Circle your choice and be able to explain your reasoning.
 - Some of the *cis*-2-pentene must isomerize and become *trans*-2-pentene.
 - The system is at equilibrium and no net reaction needs to take place.
 - Some of the *trans*-2-pentene must isomerize and become *cis*-2-pentene.

9. Consider once again the generic reversible reaction: $a \text{ A} + b \text{ B} \rightleftharpoons d \text{ D} + e \text{ E}$
- What does it mean if $Q < K_c$? (Circle your answer.)
 - Some of the reactants must react and become products until $Q = K_c$.
 - Some of the products must react and become reactants until $Q = K_c$.
 - What does it mean if $Q > K_c$? (Circle your answer.)
 - Some of the reactants must react and become products until $Q = K_c$.
 - Some of the products must react and become reactants until $Q = K_c$.

Exercise

10. Consider an aqueous solution containing oxalic acid ($[\text{H}_2\text{C}_2\text{O}_4] = 0.38 \text{ M}$), fluoride ions ($[\text{F}^-] = 4.13 \text{ M}$), hydrofluoric acid ($[\text{HF}] = 1.75 \text{ M}$) and oxalate ions ($[\text{C}_2\text{O}_4^{2-}] = 0.14 \text{ M}$):



Determine whether this system is... a.) *at equilibrium*, or b.) *if the net forward reaction is proceeding*, or c.) *if the net reverse reaction is proceeding*. Circle the correct response and Justify your conclusion with the appropriate calculation.

Model: Heterogeneous Equilibrium

If an equilibrium involves more than one phase (e.g. solid–liquid, solid–gas, liquid–gas), the reaction takes place in a *heterogeneous* system. For *liquids or solids*, experiments have shown that:

- The position of the equilibrium of a system does *not* depend on the amount of liquid or solid present in the reaction.
- Pure liquids and solids do *not* appear in the equilibrium expression.

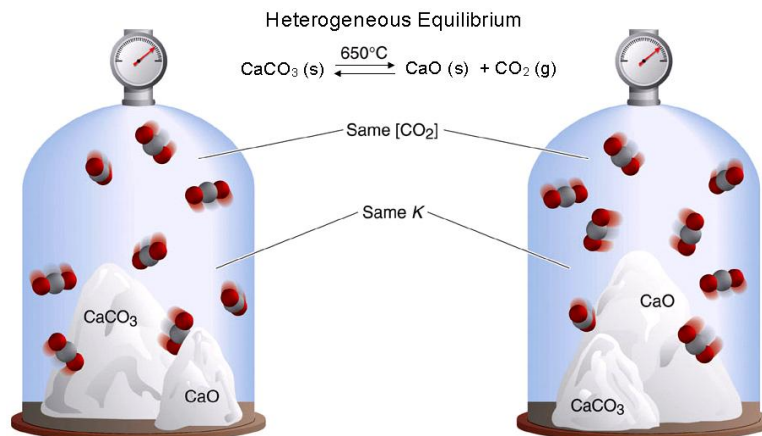
To understand why this is true, consider a simple reaction like the vaporization of water: $\text{H}_2\text{O}_{(l)} \rightleftharpoons \text{H}_2\text{O}_{(g)}$
 At a given temperature, the vapor pressure of water is a constant no matter how much liquid water there is. Thus, the position of the equilibrium does not change when you add or subtract water—therefore the equilibrium expression will *not* contain the term $[\text{H}_2\text{O}_{(l)}]$. Hence, the term for the solvent never shows up in equilibrium constant expressions for reactions that are done in that solvent—only the solute appears.

Key Questions

11. Write the law of mass action expression for the evaporation of water.

12. Consider the equilibrium between calcium carbonate, calcium oxide and carbon dioxide in the figure to the right.

- a. What effect do the *amounts* of calcium carbonate and calcium oxide have on the equilibrium? Explain why.



- b. Write the reaction quotient expression for the equilibrium: $\text{CaCO}_{3(\text{s})} \rightleftharpoons \text{CaO}_{(\text{s})} + \text{CO}_{2(\text{g})}$

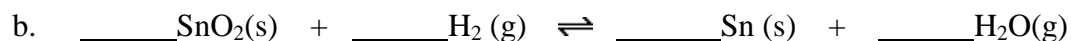
$$Q_c =$$

Exercises

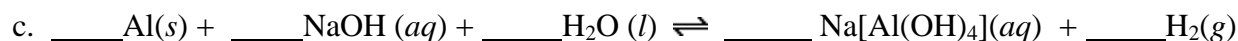
13. Balance each reaction and write its reaction quotient, Q_c .



$$Q_c =$$



$$Q_c =$$



$$Q_c =$$

14. Suppose the rate constant for the forward reaction for a particular reaction, k_{fwd} , is much smaller than the rate constant for the reverse reaction, k_{rev} . (i.e. $k_{\text{fwd}} \ll k_{\text{rev}}$)

- a. Does the reaction have a large or small equilibrium constant? Explain.

- b. Does the reaction go to completion once equilibrium is attained? Explain.