

General Chemical Equilibrium

Solving Equilibrium Problems Using the RICE-Table Method

THE NATURE OF THE EQUILIBRIUM STATE

Equilibrium is defined as the condition when the rate of the forward reaction equals the rate of the reverse reaction. Equilibrium reactions are reversible which is indicated by the presence of double arrows, \rightleftharpoons , between the reactants and the products. The double arrows indicate that the reaction is proceeding in both the forward and reverse direction and once equilibrium is established, the rate of each direction is equal (Figure 1). We also say that once equilibrium is reached, it is **dynamic**. This means reactants are forming products and products are forming reactants simultaneously such that the net concentration of each remains constant. Notice, this does NOT say the concentrations of the products and reactants are equal! That is a very common misconception.

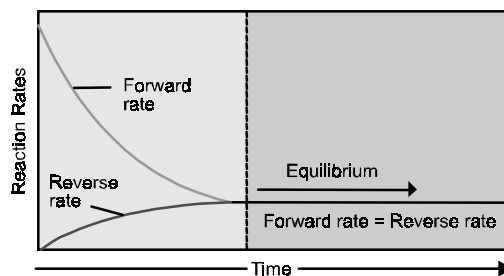
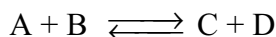


Fig. 1

Examine Figure 2 which represents the following generalized chemical reaction:



Notice that equilibrium is reached once the concentrations of the reactants and products remain constant, but again, not necessarily equal.

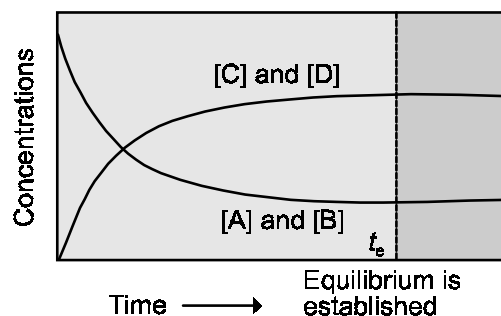


Fig. 2

What you should be able to interpret from the graphs in Figures 1 & 2:

- Equilibrium is established as soon as the curves become “flat” on either graph. This indicates a constant value has been reached for the y-axis variable.
 - For Figure 1, the rates for the forward and reverse reactions converge and the rates are equal.
 - For Figure 2, the concentrations decrease for the reactants and increase for the products until a constant value is achieved, not necessarily an equal value. The time at which equilibrium is established is denoted as $t_{\text{equilibrium}}$ or t_e .
- Equilibrium is not necessarily established at some midpoint on the graph.
 - For Figure 1, notice that the two rates did not converge at the midpoint between the two original values. The forward reaction has a much larger rate constant than the reverse reaction so it “pushes” the equilibrium position down on the graph.
 - For Figure 2, the time at which equilibrium is established can occur anywhere along the x-axis.

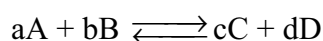
THE EQUILIBRIUM POSITION

Whether the reaction lies far to the right [products favored] or to the left [reactants favored] depends on three main factors:

- The initial concentrations of the reactants, the products, or both. The more molecules present, the more collisions that occur and the faster the reaction.
- The relative energies of reactants and products. Nature goes to minimum energy, always.
- The degree of organization of reactants and products. Nature goes to maximum disorder, always.

THE EQUILIBRIUM EXPRESSION

The first step in solving an equilibrium problem is to write the equilibrium constant expression. For the general reaction



The equilibrium constant expression, K , (a.k.a. Law of Mass Action expression) is written as follows:

$$K = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

- [] indicates concentration in molarity, M , (moles/liter)
- K_c indicates that all of the quantities in the problem are given in molarity. This applies to reactions in aqueous solution and sometimes gases.
- K_p indicates that all of the products and reactants are gases and the “p” is for partial pressures expressed in a pressure unit such as atmospheres.
- “K” values are always written without units.
- **Pure solids** do not appear in the expression
- **Pure liquids** do not appear in the expression
- **Water** does not appear in the expression since it is a pure liquid.

Pure solids and liquids, including water, do not appear in the equilibrium expression since their concentrations do not appreciably change. In other words, they are so very concentrated compared to the reactants and products in the dilute aqueous phase.

Never, ever forget that K is both a number and a relationship. You have to use both in order to be successful when working these problems.

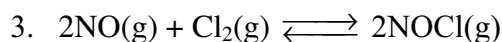
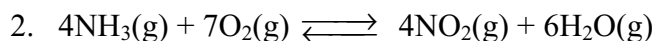
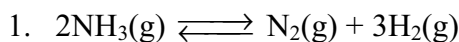
What is the significance of K ? Always remember, that generally $K = \frac{[\text{products}]}{[\text{reactants}]}$.

$K > 1$ means that the reaction **favors the products** at equilibrium. This means the concentration of the products is greater than the concentration of the reactants when the system reaches equilibrium.

$K < 1$ means that the reaction **favors the reactants** at equilibrium. This means that concentration of the reactants is greater than the concentration of the products when the system reaches equilibrium.

Example 1

Write the equilibrium expressions for the following chemical reactions:

**FACTORS AFFECTING THE VALUE OF K**

- Temperature:** As long as the temperature is constant, the numerical value of K is constant. Change the temperature, and you will have to calculate a new K.
- Changing the stoichiometric coefficients:** When the stoichiometric coefficients of a balanced equation are multiplied by some factor, the K is raised to the power of the multiplication factor, n, (K^n). Doubling the coefficients means that K is squared; tripling the coefficients means that K is cubed; cutting the coefficients in half means that you raise K to the $\frac{1}{2}$ power or take the square root of the original K, etc.
- Reversing Equations:** When the equations are reversed, simply take the reciprocal

($1/K$ or K^{-1}) of K since the general $K = \frac{[\text{products}]}{[\text{reactants}]}$ has just been “flipped”.

- Adding Chemical Reactions Together:** When equations are added together to create a summary equation, multiply the respective Ks of each equation together.
($K_{\text{summary reaction}} = K_1 \times K_2 \times K_3 \dots$)

THE RELATIONSHIP BETWEEN K_p AND K_c

Since gas quantities can be expressed in either pressure units (atm) or concentration units (mol/L), we need a way to compare K_p and K_c . Think of this as the “politically correct” equation. This helps us remember which K is listed first in the relationship so we don’t get it backwards! The equation, one worth memorizing, is:

$$K_p = K_c(\text{RT})^{\Delta n}$$

Where:

Δn = the change in the number of moles of gas as the chemical reaction is read from left to right. $\Delta n =$ (total moles gas produced) – (total moles gas reacting). Increasing the number moles of gas from left to right makes Δn a positive term, decreasing the number of moles of gas from left to right makes Δn a negative term.

R = universal gas law constant. Use the $0.0821 \frac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}}$ version of R.

T = temperature in Kelvin.

From the equation you see that $K_p = K_c$ if Δn is equal to zero since the entire (RT) term taken to the zero power becomes ONE. That means that any time the number of moles of gaseous product = number of moles of gaseous reactant, $K_p = K_c$.

A FOOL PROOF METHOD FOR SOLVING EQUILIBRIUM PROBLEMS: THE RICE-TABLE METHOD

This method of problem-solving allows you to see relationships quickly and formulate a plan of attack when faced with an equilibrium problem.

THE STEPS:

Set up your “RICE” table so that the letters **RICE** are on separate lines of your paper at the left margin:

- R** — stands for the chemical **Reaction**. Be sure it is balanced. It can be net ionic as well as molecular.
- I** — stands for **Initial** concentration [mol/L] or initial pressures in atmospheres if solving for K_p . You may have to convert information given into molarities or use a gas law to calculate a pressure in atmospheres.
- C** — stands for **Change** in concentration [mol/L] or other amounts so that this data matches your initial data. We let “x” represent unknown quantities.
- E** — stands for **Equilibrium** concentrations or other amounts. This line represents the sum of lines **I** and **C**.

From the balanced equation, write your equilibrium expression below your RICE table. Remember to omit any pure solids or liquids that may appear in the equation.

Place the initial concentrations or amounts under the appropriate reactant or product in the balanced equation, forming columns for that reactant or product. It is not uncommon for some of the “players” in the balanced reaction to start with initial concentrations or amounts of zero.

Calculate the change in concentration or amount using the coefficients from the balanced equation as the coefficients on “x”. If you lose 2 CO_2 , then you would write $-2x$ as its change in concentration or amount. If you gain 2 CO_2 , then you would write $+2x$ as its change in concentration or amount.

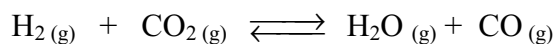
Add the “**I**” and the “**C**” rows together under each reactant or product to get an expression for the “**E**” row. Simplify the expression whenever possible.

Substitute these simplified expressions into the K expression and calculate “x”.

Return to the table and plug the value for “x” into the “**E**” line to calculate an exact concentration or amount.

Example 2

Consider the following reaction:



When $\text{H}_2(\text{g})$ is mixed with $\text{CO}_2(\text{g})$ at 1,000 K, equilibrium is achieved according to the equation above. In one experiment, the following equilibrium concentrations were measured.

$$[\text{H}_2] = [\text{CO}_2] = 0.40 \text{ mol/L}$$

$$[\text{H}_2\text{O}] = 0.20 \text{ mol/L}$$

$$[\text{CO}] = 0.30 \text{ mol/L}$$

- (a) Using the equilibrium concentrations given above, calculate the value of K_c , the equilibrium constant for the reaction.

Solution: This one is an easy start. The equilibrium concentrations were given in the problem so, proceed directly to the equilibrium constant expression.

$$K_c = \frac{[\text{H}_2\text{O}][\text{CO}]}{[\text{H}_2][\text{CO}_2]} = \frac{[0.20][0.30]}{[0.40][0.40]} = \frac{[0.06]}{[0.16]} = 0.38$$

- (b) Determine K_p , in terms of K_c for this system.

Solution: Time for the politically correct equation!

$$K_p = K_c(RT)^{\Delta n}$$

$$K_p = 0.38 \left[\left(0.0821 \frac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}} \right) (1,000 + 273\text{K}) \right]^0 = 0.38 \times 1.0 = 0.38$$

Remember, K_p only equals K_c when Δn is equal to zero since there is no change in the number of moles of gas between the products and reactants. It's quite alright to simply state $K_p = K_c$ as long as you also state that Δn is equal to ZERO.

Example 3

In a second experiment, the system in Example 2 is heated from 1,000 K to a higher temperature and the value of the equilibrium constant K_c changes. At this new temperature, $K_c = 1.5$. Calculate the equilibrium concentrations for all of the reactants and products involved in the reaction if the initial concentrations of hydrogen and carbon dioxide are both equal to 0.50M.

Solution: Construct a RICE table and insert the initial concentrations.

R:	$\text{H}_2(\text{g})$	+	$\text{CO}_2(\text{g})$	\rightleftharpoons	$\text{H}_2\text{O}(\text{g})$	+	$\text{CO}(\text{g})$
I:	0.50 M		0.50 M		0		0
C:	-x		-x		+x		+x
E:	$0.50 - x$		$0.50 - x$		$0 + x$		$0 + x$

Note:
 “I” + “C” = “E”
 for each reactant
 and product in
 the RICE table.

Plug the new equilibrium values into the K expression and set it equal to the value of K given at this new temperature:

$$K = \frac{[\text{H}_2\text{O}][\text{CO}]}{[\text{H}_2][\text{CO}_2]} = \frac{[x][x]}{[0.50 - x][0.50 - x]} = \frac{[x]^2}{[0.50 - x]^2} = 1.5$$

$$\therefore \sqrt{\frac{[x]^2}{[0.50 - x]^2}} = \sqrt{1.5}$$

$$\frac{x}{0.50 - x} = 1.2$$

$$x = 1.2(0.50 - x)$$

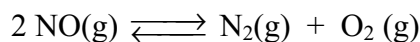
$$2.2x = 0.60$$

$$\therefore x = [0.27] = [\text{H}_2\text{O}] = [\text{CO}]$$

$$\text{and } [\text{H}_2] = [\text{CO}_2] = 0.50 - x = 0.50 - 0.27 = [0.23]$$

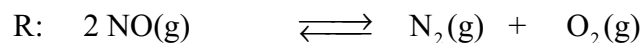
Example 4

K_c for the decomposition of nitrogen monoxide is 2.5×10^{-5} at 1,700 K.



A 0.015 mol sample of nitrogen monoxide is placed in a 12.0-L flask and heated to 1,700 K. Calculate the equilibrium concentrations of all reactants and products once equilibrium has been reached.

(a)



$$\text{I: } \frac{0.015 \text{ mol}}{12.0 \text{ L}} = 0.00125 \quad 0 \quad 0$$

$$\text{C: } -2x \quad +x \quad +x$$

$$\text{E: } 0.00125 - 2x \quad x \quad x$$

$$K_p = \frac{[\text{N}_2][\text{O}_2]}{[\text{NO}]} = 2.5 \times 10^{-5} = \frac{[x][x]}{[0.00125 - 2x]} = \frac{[x^2]}{[0.00125 - 2x]}$$

$$2.5 \times 10^{-5} (0.00125 - 2x) = x^2$$

$$3.125 \times 10^{-8} - 5.0 \times 10^{-5} x = x^2 \quad \text{set the equation equal to zero with the value for } x^2 \text{ being positive}$$

$$0 = x^2 + 5.0 \times 10^{-5} x - 3.125 \times 10^{-8} \quad \text{now you must use the quadratic formula to solve for } x.$$

It is suggested that you use a graphing calculator with a program that solves the quadratic formula.

You will get two roots, usually one will be negative, which is ridiculous since x represents a concentration. Regardless, only one of the roots will “make sense” when inserted back into your RICE table.

$$x = [\text{N}_2] = [\text{O}_2] = 1.53 \times 10^{-4} \frac{\text{mol}}{\text{L}}$$

$$[\text{NO}] = 0.00125 - 2x = 0.00122 = 1.2 \times 10^{-3} \frac{\text{mol}}{\text{L}}$$

PURPOSE

In this activity you will learn to write equilibrium constant expressions and solve equilibrium problems using the RICE-table method.

MATERIALS

calculator

paper and pencil

PROCEDURE

1. Solve the problems found on your student answer page. Be sure to show all work paying attention to the proper use of significant digits and units.

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Period _____

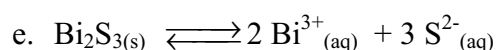
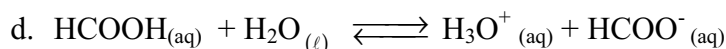
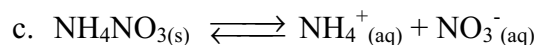
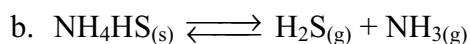
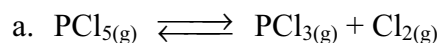
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CONCLUSION QUESTIONS

Show all work and pay special attention to significant digits and units where appropriate.

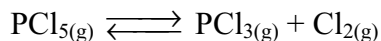
1. Write an equilibrium constant expression for each of the following unbalanced reactions: First, balance each equation, and then write the equilibrium expression leaving out pure solids and pure liquids.



2. The equilibrium constant K_p for the following reaction is 11.5 at 300°C when the amounts of reactant and products are given in atmospheres. Suppose a tank initially contains PCl_5 with a pressure of 3.00 atm at 300°C.

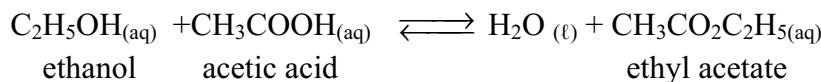
(a) What is the partial pressure of chlorine gas once equilibrium has been established?

(b) What is the value of K_c for this reaction at 300°C?

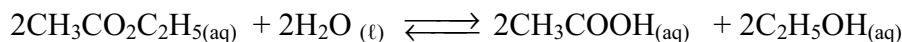


3. An aqueous solution of ethanol and acetic acid, each with a concentration 0.810 M, is heated to 125°C. At equilibrium, the acetic acid concentration is 0.645 M.

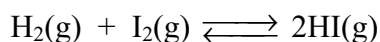
(a) Calculate K at 125°C for the reaction.



- (b) What is K for the following reaction that occurs at 125°C ?



4. The equilibrium constant for the following reaction

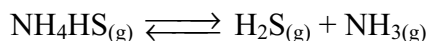


is determined to be 57.85 at 450°C .

- (a) If 1.50 mol of each reactant is placed in a 2.00-L flask at 450°C what are the concentrations of H_2 , I_2 , and HI when equilibrium has been achieved?

- (b) What is K_p for this reaction at 450°C ?

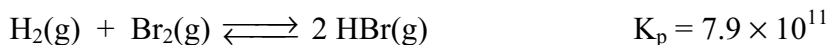
5. Ammonium hydrogen sulfide decomposes on heating.



- (a) If K_p is 0.11 at 25°C when the partial pressures are expressed in atmospheres, what is the total pressure in the flask at equilibrium?

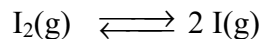
- (b) What is K_c for this reaction at 25°C ?

6. The following equilibrium constants are given at 500 K:

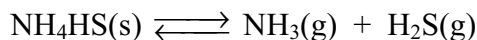


- (a) Calculate K_p for the reaction of H atoms and Br atoms to give HBr at 500 K.
- (b) Calculate K_c for this reaction at 500K.

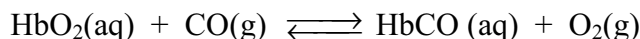
7. The equilibrium constant for the dissociation of iodine molecules to iodine atoms is 3.76×10^{-3} at 1000 K.



- (a) Suppose 0.150 mole of I_2 is placed in a 15.5-L flask at 1000K. What are the concentrations of I_2 and I when the system comes to equilibrium?
- (b) What is K_p for this reaction at 1000 K?
8. K_c for the decomposition of ammonium hydrogen sulfide is 1.8×10^{-4} at 15°C .



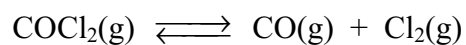
- (a) When 5.00 grams of the pure salt decomposes in a sealed 3.0-L flask at 15°C , what are the equilibrium concentrations of NH_3 and H_2S ?
- (b) What are the equilibrium concentrations at 15°C if 10.0 grams of the pure salt decomposes in the sealed flask?
9. Hemoglobin (Hb) can form a complex with both O_2 and CO. For the reaction



at body temperature, K is about 2.0×10^2 . If the ratio $\frac{[\text{HbCO}]}{[\text{HbO}_2]}$ comes close to 1.0, death is probable.

- (a) What partial pressure of CO in the air is likely to be fatal? Assume the partial pressure of O_2 is 0.20 atm.
- (b) What is K for the reverse reaction?

10. Lexan is a plastic used to make compact disks, 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



for which $K_p = 7.2 \times 10^{-11}$ at 80°C .

- (a) If pure phosgene at an initial pressure of 1.0 atm decomposes, calculate the equilibrium pressures of all species.
- (b) What is K_c for this reaction at 80°C ?