General Chemical Equilibrium
Solving Equilibrium Problems
Using the RICE-Table Method

OBJECTIVE
Students will be introduced to the concept of general equilibrium. Students will solve gas phase and concentration equilibrium problems using the RICE table problem-solving method. Students will also learn to equate $K_c$ to $K_p$.

LEVEL
Chemistry

NATIONAL STANDARDS
UCP.1, UCP.2, UCP.3, UCP.4, B.3, B.6

CONNECTIONS TO AP
AP Chemistry:
III. Reaction types  A. Reaction types  C. Equilibrium  1. Concept of dynamic equilibrium, physical and chemical; equilibrium constants  2. Quantitative treatment  b. Equilibrium constants for reactions in solution

TIME FRAME
90 minutes plus homework

MATERIALS
calculator
pencil and paper
student white boards (optional)

TEACHER NOTES
This activity is designed as a classroom lesson and will require a direct teach. Students should be guided through the general concepts and definitions of chemical equilibrium as well as the RICE-table method of problem solving. Solving stoichiometry problems using the table method presented in Lesson 16 *Stoichiometry* in this guide will provide a smooth transition for the RICE-table method of solving equilibrium problems.

There are four topics that are considered difficult in the AP* Chemistry curriculum, mostly due to the lack of exposure during the first-year chemistry course. These topics include: kinetics, equilibrium, thermodynamics and electrochemistry. This lesson is designed to introduce the basics of gas phase and concentration equilibrium. Much of what is presented here is probably absent from your high school
chemistry textbook. However, the first question in the free-response section of the AP* Chemistry exam is always an equilibrium problem. Your students will benefit from an introduction to chemical equilibrium in your first-year course.

Although the AP* exam has not yet required the use of the quadratic formula to solve an equilibrium problem, inclusion of this component will reinforce students’ algebra skills and give students that ever important connection between math and science. If students have graphing calculators available, it is advisable to install a quadratic formula solving program for their use. Students are allowed to use programmed calculators on the AP* Chemistry exam.

Many of these programs are available for free download at http://www.ticalc.org/pub/83plus/basic/math/quadratic/. This will require the use of a graph link device or calculator cable that interfaces with the computer and the free TI Connect software available at http://education.ti.com/educationportal/sites/US/productDetail/us_ti_connect.html at the time of this printing. Students are quite adept at downloading and installing programs from the computer as evidenced by the game repertoire many of their calculators possess! If you are uncomfortable with this process, make an announcement in class, and ask students to bring their calculator already programmed so they can share with other students through a calculator to calculator link.

Four examples are provided within the student pages. Answers to Example 1 are given below; all of the other examples have solutions worked out on the student pages.

a. 2 NH₃(g) ⇌ N₂(g) + 3 H₂(g)
   \[ K = \frac{[N_2][H_2]^3}{[NH_3]^2} \]

b. 4 NH₃(g) + 7 O₂(g) ⇌ 4 NO₂(g) + 6 H₂O(g)
   \[ K = \frac{[NO_2]^4[H_2O]^6}{[NH_3]^4[O_2]^7} \]

c. 2 NO(g) + Cl₂(g) ⇌ 2 NOCl(g)
   \[ K = \frac{[NOCl]^2}{[NO]^2[Cl_2]} \]
ANSWERS TO THE CONCLUSION QUESTIONS

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.
   a. \( \text{PCl}_5(g) \rightleftharpoons \text{PCl}_3(g) + \text{Cl}_2(g) \)
     \[ K = \frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]} \]
   b. \( \text{NH}_4\text{HS}(s) \rightleftharpoons \text{H}_2\text{S}(g) + \text{NH}_3(g) \)
     \[ K = [\text{H}_2\text{S}][\text{NH}_3] \]
   c. \( \text{NH}_4\text{NO}_3(s) \rightleftharpoons \text{NH}_4^+(aq) + \text{NO}_3^-(aq) \)
     \[ K = [\text{NH}_4^+][\text{NO}_3^-] \]
   d. \( \text{HCOOH}(aq) + \text{H}_2\text{O}(\lambda) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{HCOO}^-(aq) \)
     \[ K = \frac{[\text{H}_3\text{O}^+][\text{HCOO}^-]}{[\text{HCOOH}]} \]
   e. \( \text{Bi}_2\text{S}_3(s) \rightleftharpoons 2 \text{Bi}^{3+}(aq) + 3 \text{S}^2^-(aq) \)
     \[ K = [\text{Bi}^{3+}]^2[\text{S}^2^-]^3 \]
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.

$$\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$$

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

NOTE: Keep calculated values in the calculator. Rounding at each step introduces error. Carry one or two “extra” significant digits throughout the problem. Of course, round your final answer to the proper number of significant digits before reporting it.

R: PCl$_5$(g) $\rightleftharpoons$ PCl$_3$(g) + Cl$_2$(g)
I: 3.00 atm 0 0
C: $-x$ $+x$ $+x$
E: 3.00 $-x$ $x$ $x$

$$K_p = \frac{(\text{PCl}_3)(\text{Cl}_2)}{(\text{PCl}_5)} = 11.5 = \frac{(x)(x)}{(3.00 - x)} = \frac{(x^2)}{(3.00 - x)}$$

$$11.5(3.00 - x) = x^2$$

$$34.5 - 11.5x = x^2$$ set the equation equal to zero with the value for $x^2$ being positive

$$0 = x^2 + 11.5x - 34.5$$ now you must use the quadratic formula to solve for $x$.

Allow students to use a calculator program!

$$x = 2.47 \text{ atm} = P_{\text{Cl}_2} \text{ (and } 2.47 \text{ atm} = P_{\text{PCl}_3} \text{ while } P_{\text{PCl}_5} = 3.00 - x = 3.00 - 2.47 \text{ atm} = 0.53 \text{ atm})$$

b. What is the value of $K_c$ for this reaction at 300°C?

$$K_p = K_c (RT)^\Delta n; \Delta n = +1$$

$$K_c = \frac{K_p}{(RT)^\Delta n} = \frac{11.5}{(0.0821 \times 573)^{+1}} = 0.244$$
3. An aqueous solution of ethanol and acetic acid, each with a concentration 0.810 M, is heated to 125°C. At equilibrium, the ethyl acetate concentration is 0.645 M.

a. Calculate $K$ at 125°C for the reaction.

$$
\text{C}_2\text{H}_5\text{OH}(aq) + \text{CH}_3\text{COOH}(aq) \rightleftharpoons \text{H}_2\text{O}(\ell) + \text{CH}_3\text{CO}_2\text{C}_2\text{H}_5(aq)
$$

ethanol        acetic acid                  ethyl acetate

R:  $\text{C}_2\text{H}_5\text{OH}(aq) + \text{CH}_3\text{COOH}(aq) \rightleftharpoons \text{H}_2\text{O}(\ell) + \text{CH}_3\text{CO}_2\text{C}_2\text{H}_5(aq)$
I:  0.810          0.810       0
C:  $-x$           $-x$        $+x$
E:  0.810 $-x$  0.810 $-x$  $x = 0.645^*$
$0.810 - 0.645$  $0.810 - 0.645$  0.645

*$The problem stated that the equilibrium concentration of $\text{CH}_3\text{CO}_2\text{C}_2\text{H}_5$ was 0.645 M, so that IS the value of $x$.

$$
K = \frac{[\text{CH}_3\text{CO}_2\text{C}_2\text{H}_5]}{[\text{C}_2\text{H}_5\text{OH}][\text{CH}_3\text{COOH}]} = \frac{[0.645]}{[0.810 - 0.645]^2} = 23.7
$$

b. What is $K$ for the following reaction that occurs at 125°C?

$$
2 \text{CH}_3\text{CO}_2\text{C}_2\text{H}_5(aq) + 2 \text{H}_2\text{O}(\ell) \rightleftharpoons 2 \text{CH}_3\text{COOH}(aq) + 2 \text{C}_2\text{H}_5\text{OH}(aq)
$$

The second reaction is simply the original reaction reversed and doubled.

$$
\therefore K_{\text{new}} = \frac{1}{K^2} = \frac{1}{23.7^2} = 0.00178 = 1.78 \times 10^{-3}
$$
4. The equilibrium constant, \( K_c \), for the following reaction is determined to be 57.85 at 450°C.

\[ \text{H}_2(g) + \text{I}_2(g) \rightleftharpoons 2 \text{HI}(g) \]

a. If 1.50 mol of each reactant is placed in a 2.00-L flask at 450°C what are the concentrations of \( \text{H}_2 \), \( \text{I}_2 \), and \( \text{HI} \) when equilibrium has been achieved?

\begin{align*}
\text{R:} & \quad \text{H}_2(g) + \text{I}_2(g) \rightleftharpoons 2 \text{HI}(g) \\
\text{I:} & \quad \frac{1.5 \text{ mol}}{2.00 \text{ L}} = 0.750 \text{ M} \quad 0.750 \quad 0 \\
\text{C:} & \quad -x \quad -x \quad +2x \\
\text{E:} & \quad 0.750 - x \quad 0.750 - x \quad 2x \\
K & = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{[2x]^2}{[0.750 - x]^2} = 57.85
\end{align*}

Note that the expression above is a perfect square.
Simply, take the square root of both sides of the equation to solve for \( K \).

\[ \sqrt{\frac{[2x]^2}{[0.750 - x]^2}} = \sqrt{57.85} \]

\[ \frac{[2x]}{[0.750 - x]} = 7.61 \]

7.61(0.750 - x) = 2x
\[ \therefore x = 0.594 \]

\[ [\text{H}_2] = [\text{I}_2] = 0.750 - 0.594 = 0.156 \frac{\text{mol}}{\text{L}} \]

\[ [\text{HI}] = 2x = 2(0.594) = 1.19 \frac{\text{mol}}{\text{L}} \]

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

\[ K_p = K_c (RT)^\Delta n; \quad \Delta n = 0 \therefore K_p = K_c = 57.85 \]
5. Ammonium hydrogen sulfide decomposes upon heating.

\[
\text{NH}_4\text{HS}(s) \rightleftharpoons \text{H}_2\text{S}(g) + \text{NH}_3(g)
\]

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?

\[
R: \; \text{NH}_4\text{HS}(s) \rightleftharpoons \text{H}_2\text{S}(g) + \text{NH}_3(g)
\]

I: \[0 \quad 0\]

C: \[+x \quad +x\]

E: \[x \quad x\]

\[
K_p = (\text{H}_2\text{S})(\text{NH}_3) = 0.11 = x^2
\]

\[
x = \sqrt{0.11} = 0.33 \text{ atm} = P_{\text{H}_2\text{S}} = P_{\text{NH}_3}
\]

\[
\therefore P_{\text{total}} = P_{\text{H}_2\text{S}} + P_{\text{NH}_3} = 0.33 \text{ atm} + 0.33 \text{ atm} = 0.66 \text{ atm}
\]

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

\[
K_p = K_c(RT)^\Delta n; \; \Delta n = +2
\]

\[
\therefore K_c = \frac{K_p}{(RT)^\Delta n} = \frac{0.11}{(0.0821 \times 298)^2} = 1.8 \times 10^{-4}
\]
6. The following equilibrium constants are given at 500. K:

\[ \text{H}_2(\text{g}) + \text{Br}_2(\text{g}) \rightleftharpoons 2 \text{HBr}(\text{g}) \quad K_{p1} = 7.9 \times 10^{11} \]

\[ \text{H}_2(\text{g}) \rightleftharpoons 2 \text{H}(\text{g}) \quad K_{p2} = 4.8 \times 10^{-41} \]

\[ \text{Br}_2(\text{g}) \rightleftharpoons 2 \text{Br}(\text{g}) \quad K_{p3} = 2.2 \times 10^{-15} \]

a. Calculate \( K_p \) for the reaction of one mole of H atoms combining with one mole of Br atoms to yield one mole of HBr at 500. K.

To begin, rearrange the equations until you can add all three equations together to give

\[ 2 \text{H}(\text{g}) + 2 \text{Br}(\text{g}) \rightleftharpoons 2 \text{HBr}(\text{g}) \text{ as the summary or goal equation} \]

\[ \begin{align*}
\text{H}_2(\text{g}) + \text{Br}_2(\text{g}) & \rightarrow 2 \text{HBr}(\text{g}) \quad K_p = 7.9 \times 10^{11} \text{ (nothing done here, } K \text{ remains unchanged)} \\
2 \text{H}(\text{g}) & \rightarrow \text{H}_2(\text{g}) \quad K_p = 4.8 \times 10^{-41} \text{ (reversed; take reciprocal of } K) \\
2 \text{Br}(\text{g}) & \rightarrow \text{Br}_2(\text{g}) \quad K_p = 2.2 \times 10^{-15} \text{ (reversed; take reciprocal of } K) \\
\end{align*} \]

\[ \begin{align*}
2 \text{H}(\text{g}) + 2 \text{Br}(\text{g}) & \rightleftharpoons 2 \text{HBr}(\text{g}) \quad K_{p\text{new}} = 7.9 \times 10^{11} \times \frac{1}{4.8 \times 10^{-41}} \times \frac{1}{2.2 \times 10^{-15}} \\
\end{align*} \]

Next, the coefficients must be halved so the summary \( K \) is raised to the \( \frac{1}{2} \) power which is the square root of the value to give

\[ K_{p\text{new}} = \sqrt{7.9 \times 10^{11} \times \frac{1}{4.8 \times 10^{-41}} \times \frac{1}{2.2 \times 10^{-15}}} = 2.7 \times 10^{33} \]

b. Calculate \( K_c \) for this reaction at 500. K.

\[ K_p = K_c (RT)^{\Delta n}; \Delta n = -1 \]

\[ K_c = \frac{K_p}{(RT)^{\Delta n}} = \frac{2.7 \times 10^{33}}{(0.0821 \times 500.)^{-1}} = 1.1 \times 10^{35} \]
7. The equilibrium constant for the dissociation of iodine molecules to iodine atoms is \(3.76 \times 10^{-3}\) at 1000. K.

\[
I_2(g) \rightleftharpoons 2 \text{I(g)}
\]

a. Suppose 1.50 mole of \(I_2\) is placed in a 15.5-L flask at 1000. K. What are the concentrations of \(I_2\) and I when the system comes to equilibrium?

\[
\begin{align*}
\text{R:} & \quad I_2(g) \rightleftharpoons 2 \text{I(g)} \\
\text{I:} & \quad \frac{1.50 \text{ mol}}{15.5 \text{ L}} = 0.0968 \text{ M} \quad 0 \\
\text{C:} & \quad -x \quad +2x \\
\text{E:} & \quad 0.0968-x \quad 2x \\
K & = \frac{[2x]^2}{[I_2]} = \frac{[2x]^2}{0.0968-x} = 3.76 \times 10^{-3} \\
3.76 \times 10^{-3} (0.0968 - x) & = 4x^2 \\
3.64 \times 10^{-4} - 3.76 \times 10^{-3} x & = x^2 \quad \text{set equation equal to zero and use a quadratic solving program} \\
0 & = x^2 + 9.40 \times 10^{-4}x - 9.10 \times 10^{-5} \\
x & = 9.08 \times 10^{-3} \text{ mol} \text{ L}^{-1} \\
\therefore [I_2] & = 0.0968-x = 0.0968 - 9.08 \times 10^{-3} = 0.0877 \text{ mol} \text{ L}^{-1} \\
\therefore [\text{I}] & = 2x = 2(9.08 \times 10^{-3}) = 18.2 \times 10^{-2} \text{ mol} \text{ L}^{-1}
\end{align*}
\]

b. What is \(K_p\) for this reaction at 1000. K?

\[
K_p = K_c (RT)^{\Delta n}; \quad \Delta n = +1 \\
K_p = 3.76 \times 10^{-3}(0.0821 \times 1000.)^{+1} = 0.309
\]
8. $K_c$ for the decomposition of ammonium hydrogen sulfide is $1.8 \times 10^{-4}$ at 15°C.

$$\text{NH}_4\text{HS}(s) \rightleftharpoons \text{NH}_3(g) + \text{H}_2\text{S}(g)$$

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$_2$S?

R: \[ \text{NH}_4\text{HS}(s) \rightleftharpoons \text{NH}_3(g) + \text{H}_2\text{S}(g) \]

I: \[ 0 \quad 0 \]

C: \[ +x \quad +x \]

E: \[ x \quad x \]

$$K = [\text{NH}_3][\text{H}_2\text{S}] = x^2 = 1.8 \times 10^{-4}$$

$$[\text{NH}_3] = [\text{H}_2\text{S}] = \sqrt{1.8 \times 10^{-4}} = 0.013 \text{ mol/L}$$

b. What are the equilibrium concentrations of the products at 15°C if 10.0 grams of the pure salt decomposes in the sealed flask?

There was no change in temperature, so $K_c$ remains constant at $1.8 \times 10^{-4}$.

That means that the concentration of each product at equilibrium also remains constant at $0.013 \text{ mol/L}$.

The amount of solid has no effect, it is not a part of the equilibrium expression.

NOTE: The 5.00 grams in part (a) is $\approx 0.10$ moles. It is a good idea to point out to students that the total number of moles of gas formed is $\approx 0.026$ moles, so there was plenty of solid to yield the calculated number of moles of product once equilibrium was reached.
9. Hemoglobin (Hb) can form a complex with both O₂ and CO. For the reaction

\[ \text{HbO}_2(aq) + \text{CO}(g) \rightleftharpoons \text{HbCO}(aq) + \text{O}_2(g) \]

at body temperature, \( K \) is about \( 2.0 \times 10^2 \). 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 O₂ is 0.20 atm. Why is this assumption valid?

We will let \( \frac{[\text{HbCO}]}{[\text{HbO}_2]} = 1.0 \) in the equilibrium expression.

\[ \therefore K = \frac{[\text{HbCO}][\text{O}_2]}{[\text{HbO}_2][\text{CO}]} = 1.0 \left( \frac{[\text{O}_2]}{[\text{CO}]} \right) = \frac{(0.20)^*}{(0.20)} = 2.0 \times 10^2 \]

*It is a valid assumption since our atmosphere is generally 20% oxygen and 80% nitrogen.

\[ \therefore [\text{CO}] = \frac{(0.20)}{2.0 \times 10^2} = 0.0010 = 1.0 \times 10^{-3} \text{ atm} \]

b. What is \( K \) for the reverse reaction?

\[ K_{\text{reverse}} = \frac{1}{K} = \frac{1}{2.0 \times 10^2} = 0.0050 = 5.0 \times 10^{-3} \]
10. 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 (COCl₂), an extremely poisonous gas. Phosgene decomposes by the reaction

\[
\text{COCl}_2(g) \rightleftharpoons \text{CO}(g) + \text{Cl}_2(g)
\]

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.

R: COCl₂(g) \rightleftharpoons CO(g) + Cl₂(g)
I: 1.0 atm 0 0
C: \(-x\) \(+x\) \(+x\)
E: 1.0\(-x\) \(x\) \(x\)

\[
K_p = \frac{(\text{CO})(\text{Cl}_2)}{\text{COCl}_2} = 7.2 \times 10^{-11} = \frac{(x)(x)}{(1.0-x)} = \frac{(x^2)}{(1.0-x)}
\]

\[7.2 \times 10^{-11}(1.0-x) = x^2\]

\[7.2 \times 10^{-11} - 7.2 \times 10^{-11}x = x^2\]

set the equation equal to zero with the value for \(x^2\) being positive

\[0 = x^2 + 7.2 \times 10^{-11}x - 7.2 \times 10^{-11}\]

\[x = 8.5 \times 10^{-6}\text{atm} = P_{\text{Cl}_2} = P_{\text{CO}} \text{ while } P_{\text{COCl}_2} = 1.0-x = 1.0-8.5 \times 10^{-6} = 1.0\text{ atm}\]

*This is a good example of why we often neglect subtracting \(x\) when working equilibrium problems. Since \(K\) is so small, the reaction barely proceeds to the right at all. The initial pressure of the reactant at 1.0 atm is HUGE when compared to the \(x\)-value calculated with the quadratic formula. If subtracting \(x\) had been neglected, leaving the denominator as simply 1.0, then the mathematics would be simplified and \(x\) would still be equal to \(8.5 \times 10^{-6}\). It is also a matter of applying significant digit rules correctly. When subtracting \(x\) from 1.0 atm we are limited to an answer with only one decimal place, so we are essentially subtracting zero from the original pressure. More information on when to and when not to neglect \(x\) can be found in Lesson 29 Acid-Base Equilibrium in this guide.

b. What is \(K_c\) for this reaction at 80°C?

\[
K_p = K_c(RT)^{\Delta n}; \Delta n = +1
\]

\[
K_c = \frac{K_p}{(RT)^{\Delta n}} = \frac{7.2 \times 10^{-11}}{(0.0821 \times 353)^{+1}} = 2.5 \times 10^{-12}
\]
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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 reaction is equal to the other (Figure 1). We also say that once equilibrium is reached, it is \textit{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 \textit{not} say the concentrations of the products and reactants are equal! That is a very common misconception.

Examine Figure 2 which represents the following generalized chemical reaction:

\[
A + B \rightleftharpoons C + D
\]

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

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

1. 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 \textit{rates} for the forward and reverse reactions converge since the rates are equal.
   For Figure 2, the \textit{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 \( t_e \).

2. 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

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The equilibrium position of a system is defined as the set of concentrations (or pressures) established at equilibrium. Although these values may change, the mathematical value of the equilibrium constant or $K$, does not as long as the temperature is remaining constant. 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

$$aA + bB \rightleftharpoons cC + dD$$

The general equilibrium constant expression, $K$ or $K_{eq}$, (a.k.a. Law of Mass Action expression) is written as follows:

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

- Square brackets, $[ ]$, indicate concentration in molarity, $M$, (moles/liter).
- $K_c$ indicates that all of the quantities in the problem are given in molarity. The “$c$” stands for concentration. This applies to reactions in aqueous solution and sometimes gases.
- $K_p$ indicates that all of the products and reactants are gases and the “$p$” stands for partial pressures. Quantities are expressed in pressure units such as atmospheres and parentheses replace the square brackets in the equilibrium expression.
- “$K$” 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 if it is a pure liquid or a solid. Water does appear in the expression if it is in the vapor phase which is indicated by $\text{H}_2\text{O}(g)$.

Why do pure solids and pure liquids not appear in the equilibrium expression? Simple, their concentrations do not appreciably change. In other words, they are so very concentrated compared to reactants and products in the much more dilute aqueous or gas phase that even when a few molecules react it makes little impact on the total.

Never, ever forget that $K$ is both a unitless number and a relationship. You have to apply both concepts to ensure success when solving equilibrium problems.

What is the significance of $K$? Remember, that $K$ represents the ratio of products vs. reactants mathematically expressed as $\frac{[\text{products}]}{[\text{reactants}]}$. 
$K > 1$ means that the reaction \textbf{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 \textbf{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.

\textbf{EXAMPLE 1}

Write the equilibrium expressions for the following chemical reactions:

a. \[ 2 \text{NH}_3(g) \rightleftharpoons \text{N}_2(g) + 3 \text{H}_2(g) \]

b. \[ 4 \text{NH}_3(g) + 7 \text{O}_2(g) \rightleftharpoons 4 \text{NO}_2(g) + 6 \text{H}_2\text{O}(g) \]

c. \[ 2 \text{NO}(g) + \text{Cl}_2(g) \rightleftharpoons 2 \text{NOCl}(g) \]

\textbf{FACTORS AFFECTING THE VALUE OF $K$}

1. \textbf{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 $K$.

2. \textbf{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.

3. \textbf{Reversing Equations:} When the equations are reversed, simply take the reciprocal of $K$ \((1/K \text{ or } K^{-1})\) since the general equilibrium expression, \(K = \frac{\text{[products]}}{\text{[reactants]}}\), has just been “flipped”.

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

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

Where:

$\Delta n =$ 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 $\Delta n$ a positive term, decreasing the number of moles of gas from left to right makes $\Delta n$ a negative term.

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

$T =$ temperature expressed in Kelvins.

From the equation you see that $K_p = K_c$ if $\Delta n$ 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 is equal to the number of moles of gaseous reactant, $K_p = K_c$.

EXAMPLE 2

When $H_2(g)$ is mixed with $CO_2(g)$ at 1000°C, equilibrium is achieved according to the equation below.

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

In one experiment, the following equilibrium concentrations were measured.

$[H_2] = [CO_2] = 0.40 \text{ mol/L}$

$[H_2O] = 0.20 \text{ mol/L}$

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

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.

$$K = \frac{[H_2O][CO]}{[H_2][CO_2]} = \frac{0.20 \cdot 0.30}{0.40 \cdot 0.40} = \frac{0.06}{0.16} = 0.38$$
b. Determine $K_p$, in terms of $K_c$ for this system.

**Solution:** Time for the politically correct equation!

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

$$K_p = 0.38 \left[ (0.0821 \text{ L} \cdot \text{atm}/\text{mol} \cdot \text{K}) (1000 + 273 \text{ K}) \right]^0 = 0.38 \times 1.0 = 0.38$$

Remember, $K_p$ only equals $K_c$ when $\Delta n$ 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 $\Delta n$ is equal to ZERO.

**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 chemical reaction.

Place the initial concentrations or amounts under the appropriate reactant or product in the balanced reaction, forming columns for that reactant or product. It is not uncommon for some of the species 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 3**
In a second experiment, the system in Example 2 is heated from 1000°C 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 0.50 $M$.

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

<table>
<thead>
<tr>
<th>R:</th>
<th>H$_2$(g)</th>
<th>+</th>
<th>CO$_2$(g)</th>
<th>$\rightleftharpoons$</th>
<th>H$_2$O(g)</th>
<th>+</th>
<th>CO(g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I:</td>
<td>0.50 $M$</td>
<td></td>
<td>0.50 $M$</td>
<td>0</td>
<td>0</td>
<td></td>
<td>0</td>
</tr>
<tr>
<td>C:</td>
<td>$-x$</td>
<td></td>
<td>$-x$</td>
<td>+$x$</td>
<td>+$x$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>E:</td>
<td>0.50 $-x$</td>
<td>0.50 $-x$</td>
<td>0 + $x$</td>
<td>0 + $x$</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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

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

*Note*: The expression is a perfect square, so take the square root of both sides.

$$\therefore \sqrt{\frac{x^2}{(0.50-x)^2}} = \sqrt{1.5}$$

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

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

$$2.2x = 0.60$$

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

*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 $2.5 \times 10^{-5}$ at 1700 K.

$$2 \text{ NO(g)} \rightleftharpoons \text{ N}_2(g) + \text{ O}_2(g)$$

A 0.015 mol sample of nitrogen monoxide is placed in a 12.0-L flask and heated to 1700 K. Calculate the equilibrium concentrations of all reactants and products once equilibrium has been reached.

Solution:

NOTE: Keep calculated values in the calculator. Rounding at each step introduces error. Carry one or two “extra” significant digits throughout the problem. Of course, round your final answer to the proper number of significant digits before reporting it.

$$R: \quad 2 \text{ NO(g)} \rightleftharpoons \text{ N}_2(g) + \text{ O}_2(g)$$

$$I: \quad \begin{array}{ccc} \text{mol} & \text{N}_2 & \text{O}_2 \\ \frac{0.015 \text{ mol}}{12.0 \text{ L}} & 0 & 0 \end{array}$$

$$C: \quad \begin{array}{ccc} \text{mol} & \text{N}_2 & \text{O}_2 \\ -2x & +x & +x \end{array}$$

$$E: \quad 0.00125 - 2x \quad x \quad x$$

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

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

$$3.125 \times 10^{-8} - 5.0 \times 10^{-3}x = x^2$$

set the equation equal to zero with the value for $x^2$ being positive

$$0 = x^2 + 5.0 \times 10^{-3}x - 3.125 \times 10^{-8}$$

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.

$$x = [\text{N}_2] = [\text{O}_2] = 1.5 \times 10^{-4} \frac{\text{mol}}{\text{L}}$$

$$[\text{NO}] = 0.00125 - 2x = 9.4 \times 10^{-4} \frac{\text{mol}}{\text{L}}$$
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
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. You may want to load a quadratic formula solving program onto your calculator.
General Chemical Equilibrium
Solving Equilibrium Problems
Using the RICE–Table Method

CONCLUSION QUESTIONS

Use your own paper, show all work and pay special attention to significant digits and units where appropriate.

NOTE: Keep calculated values in the calculator. Rounding at each step introduces error. Carry one or two “extra” significant digits throughout the problem. Of course, round your final answer to the proper number of significant digits before reporting it.

1. Write an equilibrium constant expression for each of the following unbalanced reactions:
   a. \( \text{PCl}_5(g) \leftrightharpoons \text{PCl}_3(g) + \text{Cl}_2(g) \)
   b. \( \text{NH}_4\text{HS(s)} \leftrightharpoons \text{H}_2\text{S(g)} + \text{NH}_3(g) \)
   c. \( \text{NH}_4\text{NO}_3(s) \leftrightharpoons \text{NH}_4^+(aq) + \text{NO}_3^-(aq) \)
   d. \( \text{HCOOH}(aq) + \text{H}_2\text{O}(\lambda) \leftrightharpoons \text{H}_3\text{O}^+(aq) + \text{HCOO}^-(aq) \)
   e. \( \text{Bi}_2\text{S}_3(s) \leftrightharpoons 2 \text{Bi}^{3+}(aq) + 3 \text{S}^2^- (aq) \)

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.

\[ \text{PCl}_5(g) \leftrightharpoons \text{PCl}_3(g) + \text{Cl}_2(g) \]

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\(^\circ\)C. At equilibrium, the ethyl acetate concentration is 0.645 \( M \).
   a. Calculate \( K \) at 125\(^\circ\)C for the reaction.

   \[
   \text{C}_2\text{H}_5\text{OH}(aq) + \text{CH}_3\text{COOH}(aq) \rightleftharpoons \text{H}_2\text{O}(l) + \text{CH}_3\text{CO}_2\text{C}_2\text{H}_5(aq)
   \]

   ethanol         acetic acid        ethyl acetate

   b. What is \( K \) for the following reaction that occurs at 125\(^\circ\)C?

   \[
   2 \text{CH}_3\text{CO}_2\text{C}_2\text{H}_5(aq) + 2 \text{H}_2\text{O}(l) \rightleftharpoons 2 \text{CH}_3\text{COOH}(aq) + 2 \text{C}_2\text{H}_5\text{OH}(aq)
   \]

4. The equilibrium constant, \( K_c \), for the following reaction

   \[
   \text{H}_2(g) + \text{I}_2(g) \rightleftharpoons 2 \text{HI}(g)
   \]

   is determined to be 57.85 at 450\(^\circ\)C.
   a. If 1.50 mol of each reactant is placed in a 2.00-L flask at 450\(^\circ\)C what are the concentrations of \( \text{H}_2 \), \( \text{I}_2 \), and \( \text{HI} \) when equilibrium has been achieved?

   b. What is \( K_p \) for this reaction at 450\(^\circ\)C?

5. Ammonium hydrogen sulfide decomposes upon heating.

   \[
   \text{NH}_4\text{HS}(s) \rightleftharpoons \text{H}_2\text{S}(g) + \text{NH}_3(g)
   \]

   a. If \( K_p \) is 0.11 at 25\(^\circ\)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\(^\circ\)C?
6. The following equilibrium constants are given at 500. K:

\[ \text{H}_2(g) + \text{Br}_2(g) \rightleftharpoons 2 \text{HBr}(g) \quad K_{p1} = 7.9 \times 10^{11} \]

\[ \text{H}_2(g) \rightleftharpoons 2 \text{H}(g) \quad K_{p2} = 4.8 \times 10^{-41} \]

\[ \text{Br}_2(g) \rightleftharpoons 2 \text{Br}(g) \quad K_{p3} = 2.2 \times 10^{-15} \]

a. Calculate \( K_p \) for the reaction of one mole of H atoms combining with one mole of Br atoms to yield one mole of HBr at 500. K.

b. Calculate \( K_c \) for this reaction at 500. K.

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

\[ \text{I}_2(g) \rightleftharpoons 2 \text{I}(g) \]

a. Suppose 1.50 mole of I\(_2\) is placed in a 15.5-L flask at 1000. K. 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 \( 1.8 \times 10^{-4} \) at 15° C.

\[ \text{NH}_4\text{HS}(s) \rightleftharpoons \text{NH}_3(g) + \text{H}_2\text{S}(g) \]

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\(_2\)S?

b. What are the equilibrium concentrations of the products 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

$$\text{HbO}_2(aq) + \text{CO}(g) \rightleftharpoons \text{HbCO}(aq) + \text{O}_2(g)$$

at body temperature, $K$ is about $2.0 \times 10^2$. 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. Why is this assumption valid?

b. What is $K$ for the reverse reaction?

10. 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

$$\text{COCl}_2(g) \rightleftharpoons \text{CO}(g) + \text{Cl}_2(g)$$

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?