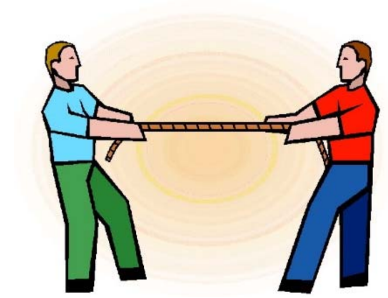
CHAPTER 15 – Chemical Equilibrium

(a) Does the picture at right best illustrate an example of **static equilibrium** or **dynamic equilibrium**?

Explain.



(b) Is Figure 11.23 on page 443 a good example of static equilibrium or dynamic equilibrium?

Explain.

(c) Look at Figure 13.8 on page on page 519. What are the two opposing processes involved? What are their relative rates in a saturated solution?

(d) According to page 611, chemical equilibrium occurs when ______________________________

____

Section 15.1 – The Concept of Equilibrium

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

(a) Consider the reaction shown above. What is the most obvious sign that this reaction involves some sort of equilibrium?

(b) What are the colors, if any, of each of the following substances?

N_2O_4 ______________________ NO_2 ______________________

(c) The tube in Figure 15.1 starts out as colorless in appearance. What chemical is present in the tube at the beginning of the experiment? ________________

(d) Over time, the appearance of the tube gradually gets darker. What is happening at the molecular level to explain why it is getting darker inside the tube?

(e) At some point, the color in the tube stops changing. A student decides that the reason that the color stops changing is because the reaction is over, and all of the N_2O_4 molecules have been converted into NO_2 molecules. Do you agree or disagree? Explain.

(f) At equilibrium, the _______________ of the forward reaction is _______________________ the ______________ of the reverse reaction.

(g) Once equilibrium has been established for a chemical reaction in a closed system, the concentrations of reactants and products ____.

However, this does not mean that the reactants and products stop reacting. Chemical equilibrium is a dynamic process, which means that ___________________________________

____

(h) Consider a general reaction that looks like this: $A \rightleftharpoons B$

Classify each of the following statements as true or false.

_______ Once equilibrium is established, [A] is equal to [B].

_______ Once equilibrium is established, k_f[A] is equal to k_r[B].

_______ Once equilibrium is established, the values of [A] and [B] are no longer changing.

_______ Once equilibrium is established, A and B are no longer reacting.

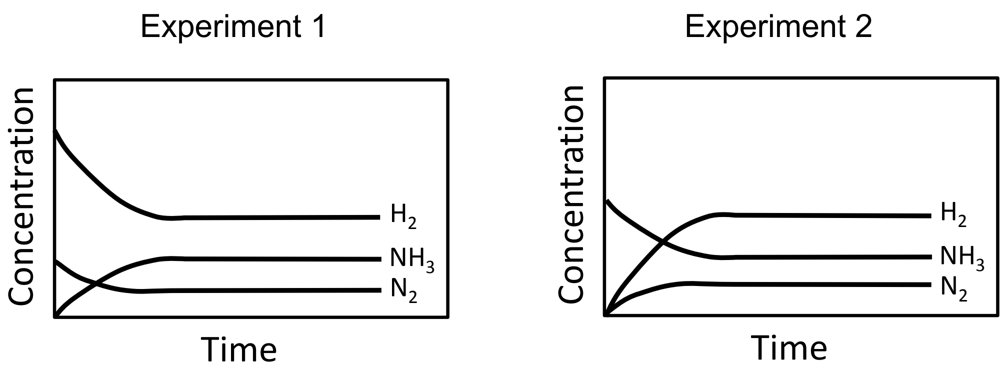
_______ Once equilibrium is established, the ratio of [B] divided by [A] equals one.

_______ Once equilibrium is established, the ratio of [B] divided by [A] equals a constant.

Section 15.2 – The Equilibrium Constant

$$N_2 \quad + \quad 3\ H_2 \quad \rightleftharpoons \quad 2\ NH_3$$

The Haber process (see above) is a reaction in which nitrogen gas and hydrogen gas react to produce ammonia. The concentration of all three substances is monitored over time in a closed system. The following diagrams were produced from two separate experiments.



(a) On each graph, draw a vertical line to indicate the time at which equilibrium has been achieved.

(b) How are Experiments 1 and 2 similar? How are they different?

(c) When equilibrium has been achieved, is it true that $[N_2] = [H_2] = [NH_3]$? _______________

(d) Write Equations 15.7 and 15.8 from page 614, which deals with the **law of mass action**.

(e) Write the equilibrium-constant expression (K_c) for each of the following chemical reactions.

(i) the Haber process

(ii) the reaction that involves the decomposition of hydrogen iodide into its elements

(f) Fill in the missing information for the change in concentration for each chemical. Use a minus sign or a plus sign with each value.

Experiment 1	N_2O_4	$\leftrightarrows$	2 NO_2
Initial Concentration (*M*)	10.00		0.00
Change in Concentration			
Equilibrium Concentration (*M*)	9.30		1.40

Experiment 2	N_2O_4	$\leftrightarrows$	2 NO_2
Initial Concentration (*M*)	0.00		10.00
Change in Concentration			
Equilibrium Concentration (*M*)	4.51		0.98

Experiment 3	N_2O_4	$\leftrightarrows$	2 NO_2
Initial Concentration (*M*)	5.00		5.00
Change in Concentration			
Equilibrium Concentration (*M*)	6.90		1.20

Experiment 4	N_2O_4	$\leftrightarrows$	2 NO_2
Initial Concentration (*M*)	10.00		5.00
Change in Concentration			
Equilibrium Concentration (*M*)	11.72		1.56

Experiment 5	N_2O_4	$\leftrightarrows$	2 NO_2
Initial Concentration (*M*)	10.00		1.00
Change in Concentration			
Equilibrium Concentration (*M*)	9.78		1.44

(g) Compare the change in NO_2 with the change in N_2O_4. What do you notice about the relative magnitude of these values?

(h) Write the equilibrium-constant expression (K_c) for the decomposition of dinitrogen tetroxide into nitrogen dioxide.

(i) Using the values for equilibrium concentrations from Experiments 1-5, calculate the value of K_c for all five experiments.

Experiment 1	N_2O_4	NO_2	K_c
Equilibrium Concentration (*M*)	9.30	1.40	

Experiment 2	N_2O_4	NO_2	K_c
Equilibrium Concentration (*M*)	4.51	0.98	

Experiment 3	N_2O_4	NO_2	K_c
Equilibrium Concentration (*M*)	6.90	1.20	

Experiment 4	N_2O_4	NO_2	K_c
Equilibrium Concentration (*M*)	11.72	1.56	

Experiment 5	N_2O_4	NO_2	K_c
Equilibrium Concentration (*M*)	9.78	1.44	

Important: The value of the equilibrium constant K_c at any given temperature does NOT depend on the initial amounts of reactants and products. The value of K_c only depends on the particular reaction and the temperature.

(j) Explain the difference between K_c and K_p.

(k) Write Equations 15.14 and 15.15 from page 617. Under what conditions would $K_c = K_p$ for a certain chemical reaction?

(l) Does the equilibrium constant (K_c or K_p) normally have units? ____________

Section 15.3 – Understanding and Working with Equilibrium Constants

(a) When the value of K is very large ($K >> 1$), the equilibrium lies to the _____________.

We say that the equilibrium is __________________–favored.

(b) When the value of K is very small ($K << 1$), the equilibrium lies to the _____________.

We say that the equilibrium is __________________–favored.

(c) Fill in the table with the missing information.

Chemical Equation	Equilibrium-Constant Expression, K_c	K_c @ 100°C
$N_2O_4(g) \rightleftharpoons 2\ NO_2(g)$		0.21
$2\ NO_2(g) \rightleftharpoons N_2O_4(g)$		

(d) The equilibrium-constant expression (K) for a reaction written in one direction is the

______________________ of the expression for the reaction written in the reverse direction.

$$H_2(g) + Cl_2(g) \rightleftharpoons 2\ HCl(g)$$

(e) The equilibrium constant for the reaction shown above is equal to 47 at 400°C. In this system, which set of chemicals is favored? How can you tell?

$$2\ HCl(g) \rightleftharpoons H_2(g) + Cl_2(g)$$

(f) What is the value of the equilibrium constant the reaction shown above at 400°C? In this system, which set of chemicals is favored? How can you tell?

(g) Fill in the table with the missing information.

Chemical Equation	Equilibrium-Constant Expression, K_c	K_c @ 100ºC
$N_2O_4(g) \rightleftarrows 2\ NO_2(g)$		0.21
$2\ N_2O_4(g) \rightleftarrows 4\ NO_2(g)$		

(h) Suppose you have an equilibrium system with a chemical equation in which the reactants are "A" and the products are "B". Now suppose that you multiply all of the coefficients in that chemical equation by some constant value, "x". How will the new value of the equilibrium constant (K_{new}) be related to the original value of $K_{original}$?

$A \rightleftarrows B$

$x\,A \rightleftarrows x\,B$

(i) Fill in the table with the missing information.

Reaction	K_c @ 400ºC
$H_2(g) + Cl_2(g) \rightleftarrows 2\ HCl(g)$	47
$\frac{1}{2}\ H_2(g) + \frac{1}{2}\ Cl_2(g) \rightleftarrows HCl(g)$	
$3\ H_2(g) + 3\ Cl_2(g) \rightleftarrows 6\ HCl(g)$	

Important: The concentrations of the substances in the equilibrium mixture will be the same no matter how you write the chemical equation. The value of K_c depends completely on how you write the reaction.

(j) What happens when you add two reactions together? Fill in the table with the missing information. Use page 621 in your textbook for the values of the equilibrium constants.

Reaction	Equilibrium-Constant Expression, K_c	K_c @ 100°C
$2\ NOBr(g) \rightleftharpoons 2\ NO(g) + Br_2(g)$		
$Br_2(g) + Cl_2(g) \rightleftharpoons 2\ BrCl(g)$		
$2\ NOBr(g) + Cl_2(g) \rightleftharpoons 2\ NO(g) + 2\ BrCl(g)$		

(k) If two (or more) chemical reactions are added together to produce a net reaction, the value of the overall equilibrium constant for the net reaction is equal to the ______________________ of the K values from each individual reaction.

(l) Given the following information:

$H_2(g) + I_2(g) \rightleftharpoons 2\ HI(g)$ $\quad K_p = 54.0$ (at 700 K)

$N_2(g) + 3\ H_2(g) \rightleftharpoons 2\ NH_3(g)$ $\quad K_p = 1.04 \times 10^{-4}$ (at 700 K)

Determine the value of K_p for the following reaction at 700 K:

$2\ NH_3(g) + 3\ I_2(g) \rightleftharpoons N_2(g) + 6\ HI(g)$

Section 15.4 – Heterogeneous Equilibria

(a) What happens when we have a chemical reaction that involves a pure solid or a pure liquid in a heterogeneous equilibrium? Do we include the concentration of that substance in the equilibrium-constant expression? ____________

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

(b) The equilibrium-constant expression for the reaction shown above is written as

K_p = ____________ or K_c = ____________

(c) As you can see in Figure 15.7 on page 623, the pressure of CO_2 in the equilibrium system at a certain temperature is __________________, no matter how much of each solid is present.

(d) Write the equilibrium-constant expression K_c for each of the following heterogeneous reactions

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

(ii) $SnO_2(s) + 2\ CO(g) \rightleftharpoons Sn(s) + 2\ CO_2(g)$

(iii) $Cr(s) + 3\ Ag^+(aq) \rightleftharpoons Cr^{3+}(aq) + 3\ Ag(s)$

(iv) $NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$

Section 15.5 – Calculating Equilibrium Constants

(a) Explain how to calculate the value of K_c if the equilibrium concentrations of all the reactants and products in a particular chemical reaction are known.

In some situations, you do not know the equilibrium concentrations of all species in an equilibrium mixture. However, if you know the initial concentrations of all species AND the concentration of at least one substance at equilibrium, you can use stoichiometry to figure out the equilibrium concentrations of every other substance in the mixture. An I-C-E chart will help you keep track of the amounts for each chemical substance throughout the pathway to equilibrium.

(b) What does I-C-E stand for? (See Sample Exercise 15.9 on page 626)

I = ___________________________

C = __________________________

E = __________________________

Note: When I make these tables, I normally put the Reaction at the top of the chart. For this reason, you will hear me refer to this as a "R-I-C-E box"

(c) Sulfur trioxide gas decomposes at high temperature in a sealed container to produce sulfur dioxide gas and oxygen gas. The reaction is an equilibrium system.

(i) Write a balanced chemical equation for this equilibrium system.

(ii) Initially, the vessel is charged at 1000 K with $SO_3(g)$ at a pressure of 0.500 atm. At equilibrium, the **total pressure** in the reaction vessel is 0.650 atm. Make a RICE box to help you calculate the pressure of all three gases in the vessel at equilibrium.

(iii) Write the equilibrium-constant expression for this reaction, and use it to calculate the value of K_p at 1000 K.

Section 15.6 – Applications of Equilibrium Constants

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

(a) Consider each of the following situations for the equilibrium system shown above. The system is allowed to reach equilibrium at 1000 K.

Initial P_{SO_3}	Initial P_{SO_2}	Initial P_{O_2}	In which direction (toward the left or toward the right) should the reaction proceed in order to reach equilibrium at 1000 K?
1.0 atm	0.0 atm	0.0 atm	
0.0 atm	1.0 atm	1.0 atm	
1.0 atm	1.0 atm	1.0 atm	

(b) Define the term reaction quotient (Q).

(c) Now consider the initial conditions in the third row of the table in part (a).

(i) What is the value of Q_p ? ____________

(ii) The value of K_p is equal to 0.338 at 1000 K.
Is Q larger than, smaller than, or equal to K_p ? ________________

(iii) In which direction will the reaction proceed in order to reach equilibrium? __________________________

(d) When comparing the value of Q to K, there are three possibilities. Indicate the direction, if any, in which the reaction would shift in order to reach equilibrium. See Figure 15.8.

If $Q = K$, ____

If $Q > K$, ____

If $Q < K$, ____

(e) Calculate Q_p for each set of given conditions and then determine in which direction the reaction will proceed in order to reach equilibrium at 1000 K. (K_p = 0.338)

Initial P_{SO_3}	Initial P_{SO_2}	Initial P_{O_2}	Q_p	In which direction (toward the left or toward the right) should the reaction proceed in order to reach equilibrium at 1000 K?
0.50 atm	1.0 atm	1.0 atm		
1.0 atm	0.50 atm	0.50 atm		
3.00 atm	1.83 atm	0.909 atm		

$$H_2(g) + I_2(g) \rightleftharpoons 2\ HI(g) \qquad K_c = 50.5 \text{ at } 448^{\circ}C$$

(f) Answer the following questions regarding the equilibrium system represented by the equation above.

(i) In an equilibrium mixture at 448°C, $[H_2] = 0.575\ M$ and $[I_2] = 0.375\ M$. Calculate the concentration of HI in this mixture.

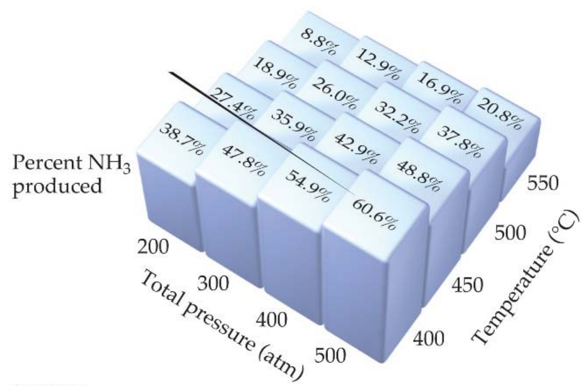
(ii) Hydrogen gas and iodine vapor were added to a previously evacuated flask. The initial concentration of each gas was equal to 2.00 *M*. The system was allowed to reach equilibrium at 448°C. Calculate the concentration of all three species present at equilibrium.

(iii) Hydrogen iodide gas was added to a previously evacuated flask. The initial concentration of $HI(g)$ was equal to 2.00 *M*. The system was allowed to reach equilibrium at 448°C. Calculate the concentration of all three species present at equilibrium.

(iv) All three gases were added to a previously evacuated flask. The initial concentration of $HI(g)$, $H_2(g)$, and $I_2(g)$ were each equal to 2.00 *M*. The system was allowed to reach equilibrium at 448°C. Calculate the concentration of all three species present at equilibrium.

Section 15.7 – Le Châtelier's Principle

(a) The diagram at right represents the % yield that is obtained from the synthesis of ammonia. Gaseous H_2 and N_2 were combined in a 3:1 molar ratio at various pressures and temperatures.



(i) As the pressure is increased from 200 atm to 500 atm, the percent yield __________________

(ii) As the temperature is increased from 400°C to 550°C, the percent yield ___________________

(b) As you can tell from part (a), an equilibrium system can be affected by various changes in pressure or temperature. Changes in concentration can also affect the equilibrium. Define Le Châtelier's principle.

$$A(g) \quad + \quad B(g) \quad \rightleftharpoons \quad C(g)$$

(c) Suppose that we have an equilibrium at 500 K between Substances A, B, and C as shown above. At equilibrium, [A] = 1.0 *M*, [B] = 2.0 *M*, and [C] = 5.0 *M*. What is the value of K_c for this reaction at 500 K? _______________

Additional B(*g*) was injected into the equilibrium mixture at 500 K until the concentration of B(*g*) became 4.0 *M*. The following RICE box has been created based on this change.

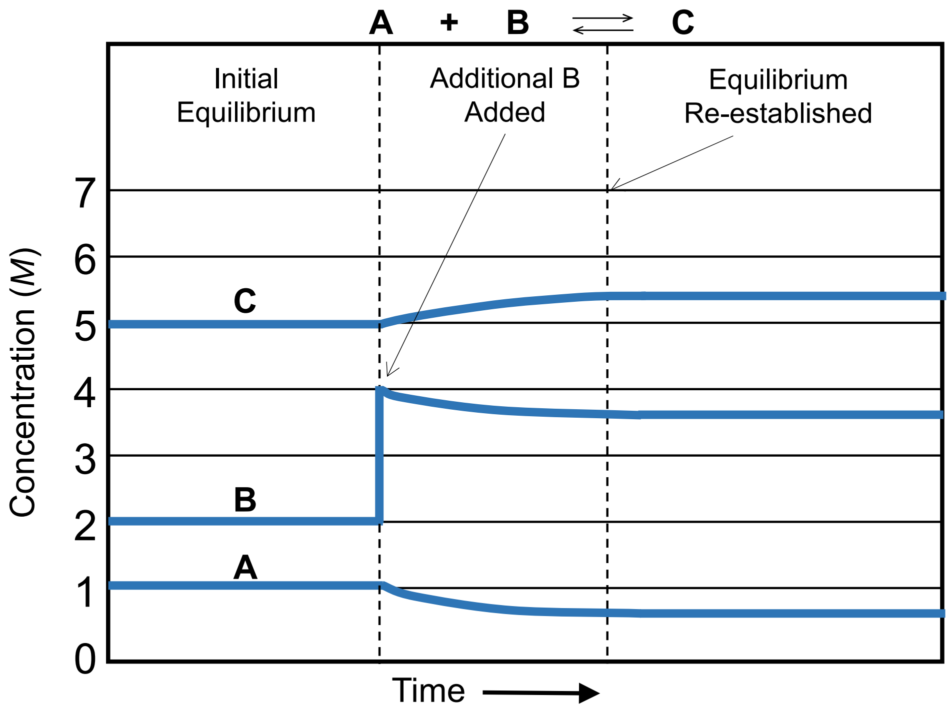
Reaction:	A	+	B	$\rightleftharpoons$	C
Initial:	1.0 *M*		4.0 *M*		5.0 *M*
Change:					
Equilibrium:					

(d) Compare Q_c to K_c. Decide if the equilibrium should shift toward the left or toward the right as a result of this change.

(e) Use the RICE box and some algebra (including the quadratic equation…sorry!) to calculate the new concentrations of A, B, and C after the equilibrium has been re-established.

Fill in the bottom row of the table below.

A	+	B	$\rightleftharpoons$	C	What's happening
1.0 *M*		2.0 *M*		5.0 *M*	system is at equilibrium at 500 K K_c = 2.5
1.0 *M*		4.0 *M*		5.0 *M*	additional B is added at 500 K Q_c = 1.25 equilibrium shifts toward the products
					system reaches a new equilibrium at 500 K K_c = 2.5



(f) Imagine that you have a system that is already at equilibrium.

If you add more reactants to the mixture, the equilibrium will shift ________________________

If you add more products to the mixture, the equilibrium will shift ________________________

If you remove reactants from the mixture, the equilibrium will shift ________________________

If you remove products from the mixture, the equilibrium will shift ________________________

When there is a shift in the equilibrium position (at constant temperature), will the value of *K* be changed? _________

The only way that the value of *K* will be changed is by changing the ______________________

(g) If an equilibrium system contains one or more gases, the volume of the container can be increased or decreased. The system will respond according to Le Châtelier's principle. See Figure 15.12

If you increase the pressure on the container by decreasing the volume, the equilibrium will shift toward the side of the equation that has ___________________________ moles of gas.

If you decrease the pressure on the container by increasing the volume, the equilibrium will shift toward the side of the equation that has ___________________________ moles of gas.

(h) Explain why changing the pressure on the equilibrium system shown below has no effect on the position of the equilibrium.

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

$$N_2O_4(g) \rightleftharpoons 2\ NO_2(g) \qquad K_c = 0.21 \text{ at } 100^oC$$

(i) Suppose that an equilibrium has been established at 100ºC such that $[N_2O_4] = 2.0\ M$ and $[NO_2] = 0.65\ M$. The volume of the container is then reduced by half at 100ºC.

Calculate the new concentration of each species at the moment the volume is reduced by half. Calculate the value of Q_c at that moment.

In which direction would the reaction
shift in order to re-establish equilibrium? ____________________

Calculate the concentration of each species when the system reaches equilibrium at 100ºC.

(j) Suppose that the pressure on the equilibrium system is increased by adding an inert gas like argon. Will the equilibrium position be affected by this change? Explain.

(k) If a reaction is endothermic, we can treat "heat" as a ______________ in the chemical equation.

If a reaction is exothermic, we can treat "heat" as a _______________ in the chemical equation.

(l) When the temperature of an equilibrium system is increased, the system responds as if we added more ____________________ to an endothermic reaction or as if we added more ____________________ to an exothermic reaction. The equilibrium will shift in the direction that consumes some of the excess heat that was added.

(m) When the temperature of an equilibrium system is decreased, the system responds as if we removed some of the ___________________ from an endothermic reaction or as if we removed some of the ___________________ from an exothermic reaction. The equilibrium will shift in the direction that produces more heat.

(n) Fill in the table below.

	Endothermic Reaction heat + R $\rightleftharpoons$ P	Exothermic Reaction R $\rightleftharpoons$ P + heat
If we increase the temperature ("adding heat")	An endothermic reaction will shift to the _____________________ and the value of K will _____________________	An exothermic reaction will shift to the _____________________ and the value of K will _____________________
If we decrease the temperature ("removing heat")	An endothermic reaction will shift to the _____________________ and the value of K will _____________________	An exothermic reaction will shift to the _____________________ and the value of K will _____________________

(o) You may recall that in part (a) of this section, it was observed that increasing the temperature of the ammonia reaction mixture caused the percent yield for the reaction to decrease. Consider the information in Table 15.2. Is the synthesis reaction for NH_3 endothermic or exothermic? Explain.

TABLE 15.2 • Variation in K_p with Temperature for $N_2 + 3\,H_2 \rightleftharpoons 2\,NH_3$

Temperature (°C)	K_p
300	4.34×10^{-3}
400	1.64×10^{-4}
450	4.51×10^{-5}
500	1.45×10^{-5}
550	5.38×10^{-6}
600	2.25×10^{-6}

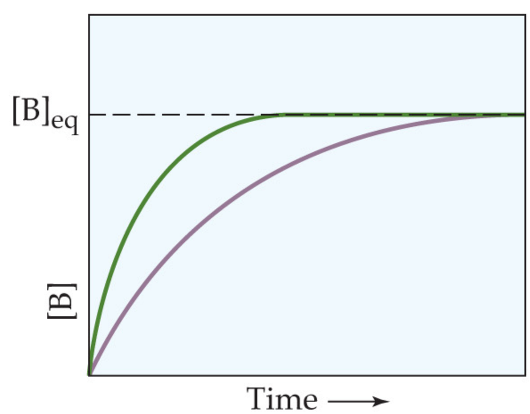
(p) A catalyst lowers the activation energy barrier. This affects the E_a value for both the forward reaction and the reverse reaction. Therefore adding a catalyst to an equilibrium system will have <u>what effect</u> of the value of *K*?

(q) Imagine a chemical equilibrium for the following

reaction: $A \rightleftharpoons B$

The diagram at right shows the change in the concentration of the product (B) over time.

One of these curves represents a catalyzed pathway and the other curve represents an uncatalyzed pathway.



Does the concentration of B change at equilibrium change as a result of a catalyst being added to the reaction?

Label each curve on the diagram as “uncatalyzed” or “catalyzed”

Explain why you made your choice.