Chapter 14 Chemical Equilibrium

Chemistry by Chang and Goldsby

Chapter 14: Chemical Equilibrium I
14.1 The Concept of Equilibrium
14.2 Writing Equilibrium Constant Expressions
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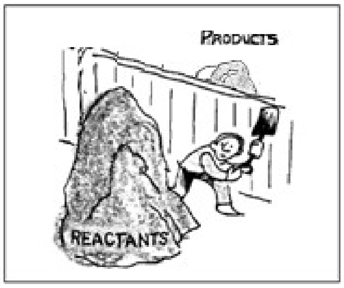
14.1 The Concept of Equilibrium and the Equilibrium Constant via a specific example.

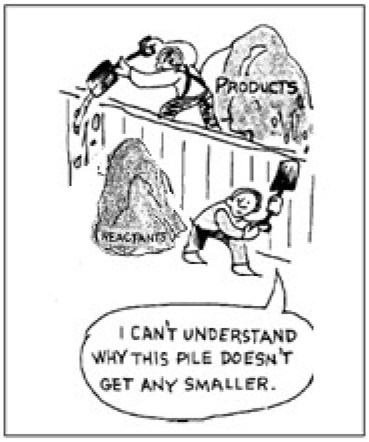
So far, we have only considered reactions where the reactants are converted to products.



However, many reactions can have products which can change back into reactants ←.
In these reactions, the forward reaction rate decreases as reactant concentrations decrease. At the same time as the product concentrations increase, the reverse reaction rate comes into play converting products back into reactants.

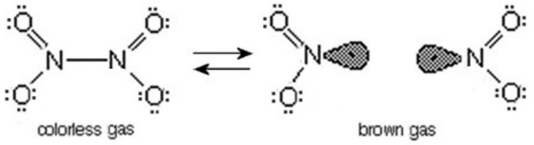
Eventually, the concentrations of reactants and products are such that

the rate of the forward reaction equals the rate of the reverse reaction.



At this point, the reaction appears to have stopped on the macroscopic scale. Yet, on the microscopic scale, the forward and reverse reactions are still proceeding.

An example of a chemically reversible reaction is $N_2O_4 \leftrightarrows 2\ NO_2$. Dinitrogen tetroxide is a colorless gas while nitrogen dioxide is a brown gas.

The Lewis dot diagrams of dinitrogen tetroxide forming nitrogen dioxide is shown in the diagram to the right.	

$$N_2O_4 \rightarrow 2\ NO_2 \quad rate_{1\rightarrow}$$
$$N_2O_4 \leftarrow 2\ NO_2 \quad rate_{2\leftarrow}$$

The rate oof these reactions are dependent on concentrations. When the system starts off with just N_2O_4, the forward $rate_{1\rightarrow}$ will predominate creating a brown gas. As N_2O_4 is consumed, its concentration will be lowered decreasing the forward reaction rate. Simultaneously the NO_2 concentration will increase causing $rate_{2\leftarrow}$ to increase.
Eventually, the concentrations or the reactants and products will be such that the forward rate and the reverse rates are equal.

$$N_2O_4 \rightleftarrows 2\ NO_2$$
$$rate_{1\rightarrow} = rate_{2\leftarrow}$$

At equilibrium, the forward rate equals the reverse rate!

When the reaction is at equilibrium the concentrations of reactants and products remain constant and the reaction appears to have stopped. Yet NO_2 molecules will still be making bonds and releasing kinetic energy, and N_2O_4 will continue to break bonds, absorbing kinetic energy. When the rates of the opposing reactions are equal, there is no change in concentration or temperature.

A DYNAMIC EQUILIBRIUM exists in a reversible reaction when the rate of the forward reaction is equal to the rate of the reverse reaction.

This cartoon would make sense to someone who understands the dynamic nature of reaction equilibrium.[1]	
	
At equilibrium there are no macroscopic (visible) changes.	Yet on the molecular level both forward and reverse reactions are occurring.

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[1] Sidney Harris Science Cartoons: http://www.sciencecartoonsplus.com/

While the rates of reaction must be equal at equilibrium, the **concentrations do not have to be equal** at equilibrium.
To determine the concentrations once a system is at equilibrium requires the use of the equilibrium expression.

The concentrations of substances **at equilibrium** can be predicted by the **Equilibrium Expression**.
There are two possible equilibrium expressions.
One expression is for solution concentrations with units of molarity and the other is with gas pressures with units of atm.

In a solution, [brackets] stand for molarity.	In a gas, (parentheses) stand for partial pressures in atm.
$K_c = \frac{[C_{products}]}{[C_{reactants}]}$	$K_P = \frac{(P_{products})}{(P_{reactants})}$ If you use concentration brackets, [ ], in a gas equilibrium expression, K_p, your answer will be marked as incorrect on the AP Chem exam.

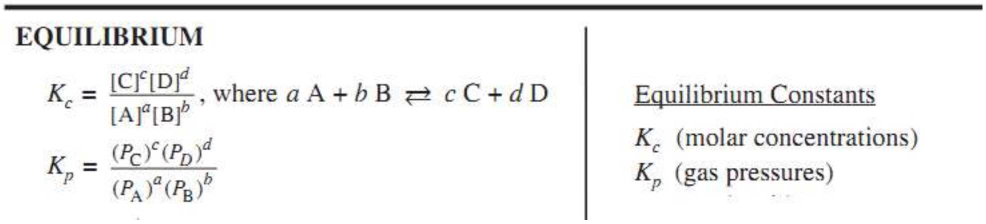
The conversion equation for the molar concentration-gas equilibrium constants is not part of the AP Curriculum.

In both cases, the equilibrium constant, ***K*, does not have units**.

This is one of the few cases where a constant does not have units.

Do not confuse the italicized capital *K* unit-less equilibrium constant with the italicized lower-case *k* rate constant which always has units.

14.2 Writing Equilibrium Constant Expressions



EQUILIBRIUM

$K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$, where $a\text{ A} + b\text{ B} \rightleftarrows c\text{ C} + d\text{ D}$

$K_p = \frac{(P_C)^c(P_D)^d}{(P_A)^a(P_B)^b}$

Equilibrium Constants

K_c (molar concentrations)

K_p (gas pressures)

Products over reactants raised the power of the coefficients of the balanced reaction.

The equilibrium constant expressions for the reaction written as $N_2O_4 \leftrightarrows 2\ NO_2$ would be:

Concentration Equilibrium Expression	Gas Pressure Equilibrium Expression[2]
$K_c = \frac{[NO_2]^2}{[N_2O_4]}$ molar concentration because of the [ ] $K_c = 4.6\times10^{-3}$ @ 25°C	$K_p = \frac{(P_{NO_2})^2}{(P_{N_2O_4})}$ atm is the default unit of pressure and uses parentheses with the *P* rather than brackets for the equilibrium expression. $K_p = 0.11$ @ 25°C Using brackets in a gas pressure equilibrium expression is incorrect!

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[2] The $K_c \neq K_p$ for this reaction. $K_c = K_p$ only when the moles of gas in the sum of the coefficients of the products equals the sum of the coefficients in the reactants.

Heterogeneous Equilibria

DO NOT INCLUDE SOLIDS (*s*) OR LIQUIDS (*l*) IN THE EQUILIBRIUM EXPRESSION!

The amount of pure solid or pure liquid is irrelevant to the Equilibrium Expression. Since there is no change in concentration in a pure solid or pure liquid, the amount of solid or liquid will not be involved in an equilibrium expression equation.

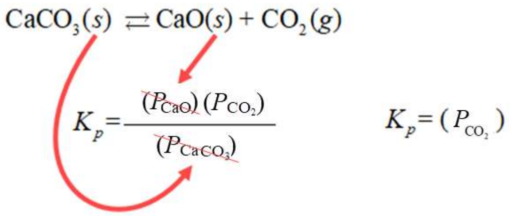
Equilibrium concentration and pressure calculations only involve (*aq*) and (*g*) species because (*aq*) and (*g*) species molar concentrations and pressures can be changed.

Look out for the exception to the rule:
There is a special situation where $H_2O(l)$ can be involved in an equilibrium.
In non-aqueous solutions, water's concentration can be altered to affect an equilibrium.
In these special cases where water's concentration can be changed $H_2O(l)$ is included in the equilibrium expression.
The only time this has shown up on the AP exam was with an alcohol solution where water was listed as $H_2O(l)$ in the mixture. The question said that the equilibrium was in a "nonaqueous system".

Example of a non-inclusion of solids in an equilibrium:

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

The equilibrium expression for the above reaction has only one gaseous concentration in its equation.

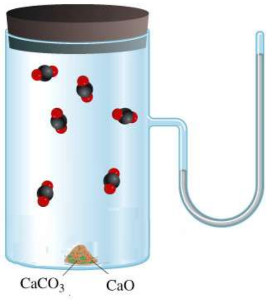
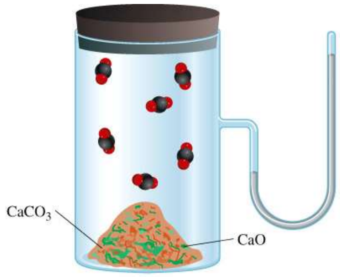


$$CaCO_3(s) \rightleftarrows CaO(s) + CO_2(g)$$

$$K_p = \frac{\cancel{(P_{CaO})}(P_{CO_2})}{\cancel{(P_{CaCO_3})}} \qquad K_p = (P_{CO_2})$$

A sealed sample of calcium carbonate would decompose into calcium oxide powder and carbon dioxide gas. However, the concentration of the gas is not dependent on the amount of carbonate or oxide if there is enough of each solid to maintain the equilibrium.

In a sealed container, the carbon dioxide pressure, (P_{CO2}), will remain the same for a given temperature no matter how much calcium carbonate or calcium oxide is added.

	
$CaCO_3(s) \rightleftarrows CaO(s) + CO_2(g)$ This amount of calcium carbonate and calcium oxide produces a certain carbon dioxide pressure in the closed container on reaching equilibrium. The equilibrium constant will equal the carbon dioxide vapor pressure: $K = (CO_2)$	$CaCO_3(s) \rightleftarrows CaO(s) + CO_2(g)$ A larger amount of calcium carbonate and calcium oxide produces the **same carbon dioxide pressure** on reaching equilibrium. The equilibrium expression is still: $K = (CO_2)$ and the equilibrium expression is unchanged.

Rules for calculating *K* when the reaction equations are changed or combined.

When a reversible reaction is reversed, the new equilibrium constant is equal to the reciprocal of the original.

$A + B \rightleftarrows C \qquad K = 7.0 \times 10^{-3}$

$$C \rightleftarrows A + B \qquad K = \frac{1}{7.0 \times 10^{-3}} = 140$$

When a reaction is doubled, the equilibrium constant will be squared.

$A + B \rightleftarrows C \qquad K = 7.0 \times 10^{-3}$

$2\,A + 2\,B \rightleftarrows 2\,C \qquad K = 4.9 \times 10^{-5}$

When reactions are added to make a new reaction, their equilibrium constants are multiplied.

Reaction 1	$A + B \rightleftarrows C$	$K_1 = 7.0 \times 10^{-3}$
Reaction 2	$C + D \rightleftarrows E$	$K_2 = 2.0 \times 10^{-2}$
Reaction 1 + Reaction 2	$A + B + D \rightleftarrows E$	$K = K_1 \times K_2 = 1.4 \times 10^{-4}$

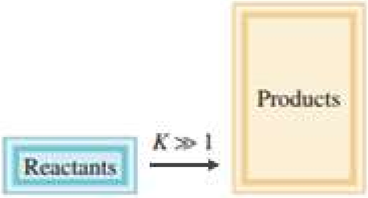
14.3 The Relationship Between Chemical Kinetics and Chemical Equilibrium

Skip this section as it is not required in AP Chemistry.

14.4 What Does the Equilibrium Constant Tell Us?

Large equilibrium constants: *K* >>1 $\quad K = \frac{[\text{Products}]}{[\text{reactants}]}$

With a large equilibrium constant, at equilibrium, concentrations of reactants will be low and concentrations of products will be high.

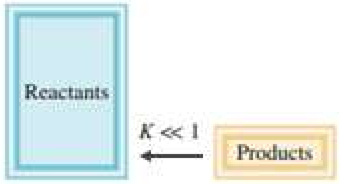


When $K > 10^6$, you can typically **ignore the equilibrium expression equation** and use simple stoichiometry to solve the problem. This will make the problem easy to solve.

It is not unusual for an AP question to have a reaction given with an equilibrium symbol, ⇆, and K_{eq} as part of the problem even though the reaction is a simple → stoichiometry problem and there will be no need to go through the complex equilibrium calculations.

Small equilibrium constants: *K* <<1 $\quad K = \frac{[\text{products}]}{[\text{Reactants}]}$

With a small equilibrium constant, at equilibrium, concentrations of reactants will be high, and concentrations of products will be low.



While the equilibrium constant tells you about the relative concentrations of the products and reactant**s, it will not tell you how quickly the reaction will reach equilibrium. A reaction with a large equilibrium constant might reach equilibrium in a fraction of a second or it may require centuries to reach equilibrium.**

N.B. **Catalysts do not change the K_{eq}**

The equilibrium concentrations and pressures of a catalyzed reaction are no different than the uncatalyzed reaction.
Both the forward and reverse reaction rates are increased by the catalyst.
A catalyst only allows a reaction to reach equilibrium sooner.

Uncatalyzed rxn: $A \rightleftarrows B$ Catalyzed rxn: $A \underset{catalyst}{\overset{catalyst}{\rightleftarrows}} B$

$K_{eq} = x$ $K_{eq} = x$

Predicting the Direction of a Reaction, the **reaction quotient test, *Q***

Q* is the Reaction Quotient.** ***Reaction Quotient $Q = \dfrac{[C]^c[D]^d}{[A]^a[B]^b}$

The reaction quotient, Q, is a test situation where you plug in the existing conditions.
If the reaction quotient equals the equilibrium constant, $Q = K_{eq}$, the reaction is at equilibrium.
If the reaction quotient is not equal to the equilibrium constant, $Q \neq K_{eq}$, the reaction will shift in to reach the equilibrium.
The table below shows how to use the reaction quotient to examine an equilibrium problem.

If $Q < K$, the Q must increase, $\dfrac{[\text{Products}]\uparrow}{[\text{Reactants}]\downarrow}$ and the forward reaction rate will be greater until $Q = K$

If $Q > K$, the Q must decrease, $\dfrac{[\text{Products}]\downarrow}{[\text{Reactants}]\uparrow}$ and the reverse reaction rate will be greater , until $Q = K$

When $Q = K$, equilibrium has been reached€ and there will be no changes from the given concentrations.

This mnemonic will help you remember the principle:

The reaction will shift in the direction of the alligator.


Reaction proceeds to the right!


Reaction proceeds to the left!

When given an equilibrium problem with concentrations, calculate the Reaction Quotient, Q.
The reaction will shift so that the concentrations have adjusted so that $Q = K$.

Equilibrium is only present when $Q = K$.

RICE Table Stoichiometric Rules and Equilibria

If the equilibrium constant is very large (10^6 or more), the reaction is pretty much just a simple →which goes to completion. Just use a simple RICE table where the reactants change into products, following stoichiometric ratios and the RICE table rules.

Don't use the equilibrium expression when the equilibrium constant is 10^6 just follow your regular stoichiometric RICE charts were the reaction →

Balanced **R**xn with coefficients	aA	→	bB
Initial moles	*x*		*y*
Change in moles (follows coefficient ratios)	-*x*		+ *z* follow the stoichiometry
End moles (sum of initial and change)	0		*y* + *z*

There are numerous ways that stoichiometry problems involving equilibrium concentrations can be presented.
If you understand the basics of RICE table stoichiometry, the equilibrium expression, and algebra, you will find a way of solving these problems. The following two examples are typical. WebAssign will show the types of equilibrium problems that have been used on AP Chemistry exams.

Ethyl ethanoate, aka ethyl acetate ($CH_3COOC_2H_5$), can be formed by the reaction of ethene (C_2H_4) with ethanoic acid (CH_3COOH) in an inert solvent according to the equation

$$C_2H_4 + CH_3COOH \rightleftarrows CH_3COOC_2H_5$$

(a) Write an expression for the equilibrium constant K_c in terms of the concentrations of the mixture

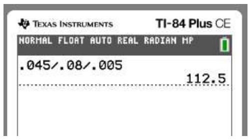
$$K_c = \frac{[CH_3COOC_2H_5]}{[C_2H_4][CH_3COOH]}$$

(b) In an experiment to produce some ethyl ethanoate, 0.050 moles of ethene was mixed with 0.020 moles of ethanoic acid. An inert solvent was used to produce 400. mL of solution. When equilibrium was established, the mixture was found to contain 0.018 moles of ethyl ethanoate.

(i) Calculate the number of moles of ethene and ethanoic acid present at equilibrium.
(ii) Calculate the molar concentration of all three substances present at equilibrium.
(iii) Calculate the value of K_c for the reaction under these conditions.

Rxn	C_2H_4	+	CH_3COOH	⇄	$CH_3COOC_2H_5$
Initial mol	0.050		0.020		0.00
Change mol	-0.018		-0.018		0.018
Equilibrium mol	0.032		0.002		0.018
Vol in L	0.400		0.400		0.400
[Equilibrium] mol L^{-1}	0.080		0.005		0.045

$$K_c = \frac{[CH_3COOC_2H_5]}{[C_2H_4][CH_3COOH]} = \frac{[0.045]}{[0.080][0.005]} = 100$$



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.045/.08/.005
                    112.5
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The equilibrium constant, K_c, for the reaction below has a value of 60. at 450°C.

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

2.0 moles of hydrogen and 2.0 moles of iodine are placed into a 15.7 L container at 450°C.

(a) Calculate the reaction quotient, Q, and describe the equilibrium state of this mixture.

$$Q = \frac{[HI]^2}{[H_2][I_2]} \qquad Q = \frac{\left[\frac{0}{15.7\text{ L}}\right]^2}{\left[\frac{2.0}{15.7\text{ L}}\right]\left[\frac{2.0}{15.7\text{ L}}\right]} \qquad Q = \frac{\left[\frac{0}{\cancel{15.7\text{ L}}}\right]\left[\frac{0}{\cancel{15.7\text{ L}}}\right]}{\left[\frac{2.0}{\cancel{15.7\text{ L}}}\right]\left[\frac{2.0}{\cancel{15.7\text{ L}}}\right]} \qquad Q = 0$$

When the number of moles of product equals the number of moles of reactant in the balanced reaction (in this case, 1 + 1 → 2), the volume aspect of the reaction cancels, and moles rather than molar concentration can be used in equilibrium expression calculations. This is a useful shortcut that can save valuable time on a test.

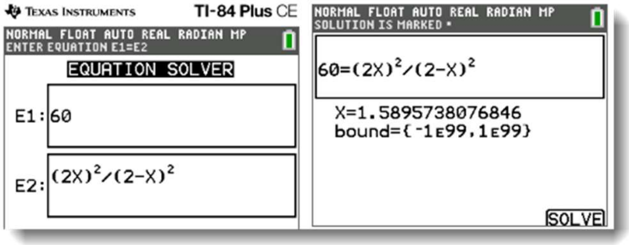
(b) Calculate the concentrations of each of the components when equilibrium in this container is reached at 450°C.

$Q < K$ so the reaction will progress → to make more product until $Q = K$

Rxn	H_2	+	I_2	$Q < K$ → Follow the alligator	2 HI
Initial mol	2.0		2.0		0.00
Change mol	$-x$		$-x$		$+2x$
Equilibrium mol	$2.0 - x$		$2.0 - x$		$2x$

$$K_c = \frac{[HI]^2}{[H_2][I_2]}$$

$$60. = \frac{[2x]^2}{[2.0 - x][2.0 - x]} = \frac{[2x]^2}{[2.0 - x]^2}$$



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TEXAS INSTRUMENTS TI-84 Plus CE
NORMAL FLOAT AUTO REAL RADIAN MP
ENTER EQUATION E1=E2
EQUATION SOLVER
E1:60
E2:(2X)²/(2-X)²
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NORMAL FLOAT AUTO REAL RADIAN MP
SOLUTION IS MARKED ▪
60=(2X)²/(2-X)²
X=1.5895738076846
bound={-1E99,1E99}
SOLVE
```

At equilibrium, the mol amounts and concentrations for all the species would be:

Rxn	H_2	+	I_2	→	2 HI
Equilibrium mol	$2.0 - x$		$2.0 - x$		$2x$
Equilibrium mol	2.0 – 1.59		2.0 - 1.59		2 × 1.59
Equilibrium mol	0.41		0.41		3.18
[Equilibrium]	$\frac{0.41\text{ mol}}{15.7\text{ L}} = 0.026M$		$\frac{0.41\text{ mol}}{15.7\text{ L}} = 0.026M$		$\frac{3.18\text{ mol}}{15.7\text{ L}} = 0.20M$

With these new amounts, $Q = 60 = K$, the system is at equilibrium.

14.5 Factors That Affect Chemical Equilibrium, Le Châtelier's Principle

¡ Important caveat on the use of Le Châtelier's principle!

> **Except for temperature changes, DO NOT USE Le Châtelier as an explanation in FRQ questions.**
> While Le Châtelier's principle is a fast way to predict changes in equilibrium situations, Le Châtelier's Principle cannot be used as an explanation for equilibrium shifts in FRQ questions.
> The only accepted method of explaining or justifying equilibrium shifts for FRQ's requires the use of Q and K

Le Châtelier's Principle is useful because it can be used in MC problems to quickly predict what will happen when a system at equilibrium is perturbed without having to go through the equilibrium expression and the reaction quotient.

Le Châtelier's Principle In any equilibrium when a change is made to some external factor such as temperature, pressure, or concentration, the equilibrium shifts to offset the change. 1888, le principe de Le Châtelier.	 Henry Le Châtelier

Monsieur Le Châtelier can help you predict the response to changes to systems at equilibrium caused by:

1. **Adding or removing a reactant or product**

2. **Changing the volume of the container with a gaseous reactant or product.**

3. **Temperature changes** (The only factor that will change the value of K and is allowable in FRQ's).

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1. Adding or removing a reactant or product so that a concentration changes.

Le Châtelier's principle predicts that a reaction will shift away from the increased concentration and towards any decrease in concentration.

e.g. HF ionizes in water according to the following equation.

$$HF(aq) \rightleftarrows H^+(aq) + F^-(aq) \text{ at room temperature the } K_c = 9 \times 10^{-4}.$$

The mixture has reached equilibrium then NaF(s) is added to the mixture. On dissolving the [F^-] increases, stressing the equilibrium by increasing a product concentration.

$$HF(aq) \rightleftarrows H^+(aq) + \mathbf{F^-(aq)} \uparrow$$

The reaction will shift to relieve that stress by increasing the rate of the reverse reaction.

$$HF(aq) \leftarrow H^+(aq) + \mathbf{F^-(aq)}$$

A new equilibrium will be reached with a decrease in [H^+] and [F^-] and increase in [HF].

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2. Changing the volume of the container with a gaseous reactant or product.

Increasing the concentration of individual gases by injecting the gases into the container follows the Le Châtelier rules which are covered in rule 1. However, changing pressures by **changing the volume of the container** involves all the gases in the equilibrium equally.

Any shift depends on the coefficients of gaseous substances, (*g*), in the balanced reaction.

A **decrease in the volume of the container** increases the pressure of all the gases and the reaction shifts to **favor the side of the reaction with the smaller number of moles of gas**.

An **increase in the volume of the container** decreases the pressure of all the gases and the reaction shifts to **favor the side with the larger number of moles of gas.**

If the **sum of the coefficients of the reactant gases = the sum of the coefficients of the product gases**, changes in the volume of the container in a gaseous system at equilibrium will have **no effect** in shifting the equilibrium.

Increasing pressure by adding an inert gas will not cause a shift in equilibrium.
The addition of an inert gas, while increasing total pressure, will not alter the partial pressures of the reacting gases. **Be on the lookout for this special situation as it is a common "trick question" on AP Chem exams**.

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3. Temperature changes

Temperature change is the only factor that will change the value of *K*.
This is the only type if equilibrium shift that allows using Le Chât rather than *Q* as an explanation in FRQ's.

Temperature changes can be answered by thinking of heat as a reactant or a product of a chemical reaction.

Heat is a product of exothermic reactions: **Exothermic reactions: A ⇄ B + Heat**

Heat is consumed as a reactant in endothermic reactions: **Endothermic reactions: Heat + A ⇄ B**

Once you have added "heat" to the equation of an equilibrium reaction, you can apply Le Châtelier's principle.

Exothermic reactions, A ⇄ B + Heat

Increases in Temperature	Decreases in Temperature
Stress: **A ← B +** $T_{\text{increased}}$ ↑	Stress: **A → B +** $T_{\text{decreased}}$ ↓
shift to make more reactants ←	*Shift to make more products →*
decreases K_{eq}	**K_{eq} increases**

Endothermic reactions, Heat + A ⇄ B

Increases in Temperature	Decreases in Temperature
Stress: $T_{\text{increased}}$ ↑ **+ A → B**	Stress: $T_{\text{decreased}}$ ↓ **+ A ← B**
shift to make more products →	*shift to make more reactants ←*
K_{eq} increases	**decreases K_{eq}**

This Le Chât explanation is a convenient trick. The reason for the shift is more complex involving the differences between the activation energy of forward and reverse reactions and is not part of AP Chemistry.