

Chapter 6: Chemical Equilibrium

6.1 The Equilibrium Condition

6.2 The Equilibrium Constant

6.3 Equilibrium Expressions Involving Pressures

6.4 The Concept of Activity

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6.6 Applications of the Equilibrium Constant

6.7 Solving Equilibrium Problems

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6.9 **OMIT:** Equilibria Involving Real Gases

The Equilibrium Constant - Definition

Consider the generalized chemical reaction:



A, B, C and D represent chemical species and a , b , c , and d are their stoichiometric coefficients in the balanced chemical equation. At equilibrium,

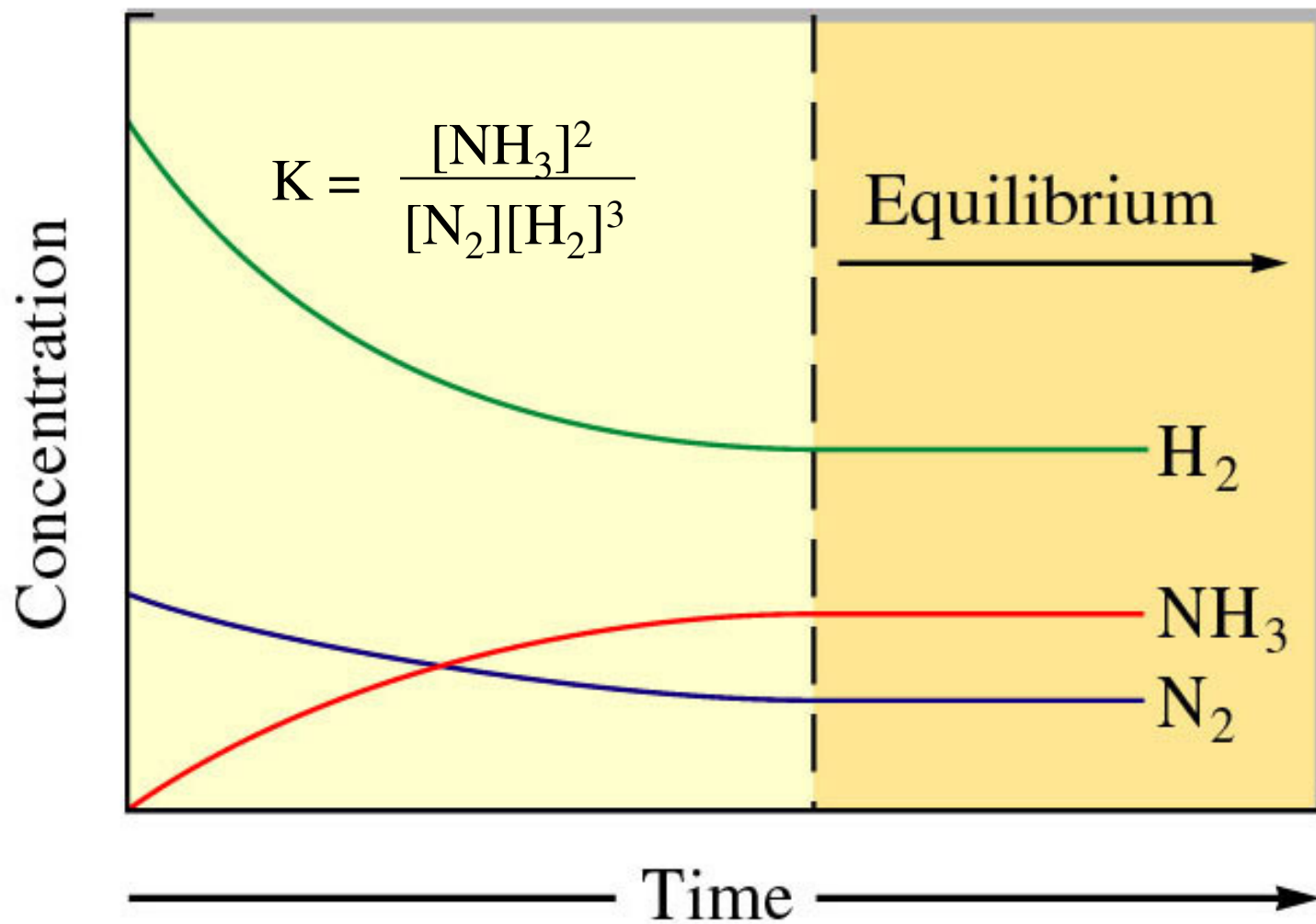
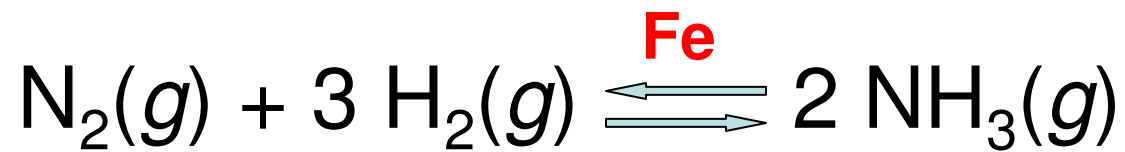
$$K = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

Note: The “units” for K are concentration units raised to some power = $c+d-(a+b)$

The square brackets indicate the concentrations of the species in equilibrium.

K is a constant called the **equilibrium constant**.

K depends only on T , and not on concentrations.



Example: Calculating Equilibrium concentrations from K and initial conditions.

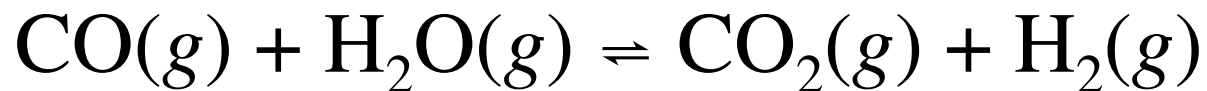
Consider the equilibrium: $\text{CO}(g) + \text{H}_2\text{O}(g) \rightleftharpoons \text{CO}_2(g) + \text{H}_2(g)$

0.250 mol CO and 0.250 mol H₂O are placed in a **125 mL** flask at 900 K. What is the composition of the equilibrium mixture if **K = 1.56**?

The original reactant concentrations are:

$$[\text{CO}]_0 = [\text{H}_2\text{O}]_0 = 0.250 \text{ mol} / 0.125 \text{ L} = 2.00 \text{ M}$$

$Q = 0$. Therefore, $Q < K$, so reactants are consumed and products made.



Conc. (M)	$\text{CO}(g)$	$\text{H}_2\text{O}(g)$	$\text{CO}_2(g)$	$\text{H}_2(g)$
I nit. [i]	2.00	2.00	0	0
C hange = X times coefficient = neg. for reactants	-X	-X	+X	+X
E qbm. [i] = Init.+Change	2.00 - x	2.00 - x	0+x = x	0+x = x

Called an “**I.C.E.**” table.

Substitute $[i]_{\text{eqbm}}$ into the equilibrium expression:

$$K = \frac{[\text{CO}_2][\text{H}_2]}{[\text{CO}][\text{H}_2\text{O}]} = \frac{(x)(x)}{(2.00-x)(2.00-x)} = \frac{x^2}{(2.00-x)^2} = 1.56$$

Taking the square root of both sides:

$$\frac{x}{2.00-x} = \sqrt{1.56} = \pm 1.25$$

Since only the positive root meaningful, ignore the negative root:

$$1.25 = \frac{x}{2.00-x}$$

$$x = 1.11 \text{ M}$$

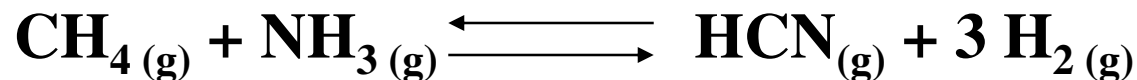
Le Chatelier's Principle

If a change in conditions (a 'stress' such as change in P, T, or concentration) is imposed on a system at equilibrium, the equilibrium position will shift in a direction that tends to reduce that change in conditions.

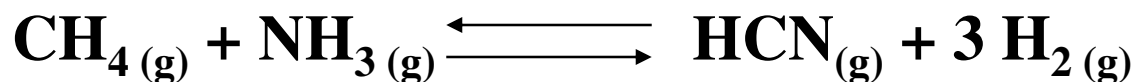
Henri Le Chatelier, 1884

The Effect of a Change in Concentration–I

Given an equilibrium equation such as :



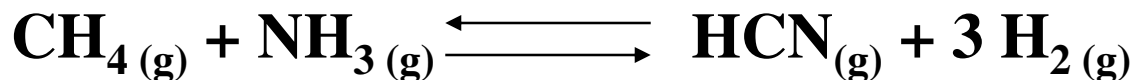
If one adds ammonia to the reaction mixture at equilibrium, it will force the reaction to go to the right producing more product. Likewise, if one takes ammonia from the equilibrium mixture, it will force the reaction back to produce more reactants by recombining H_2 and HCN to give more of the initial reactants, CH_4 and NH_3 .



Add NH_3



Forces equilibrium to produce more product.

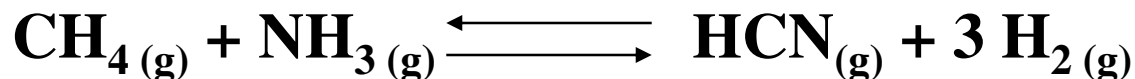


Remove NH_3

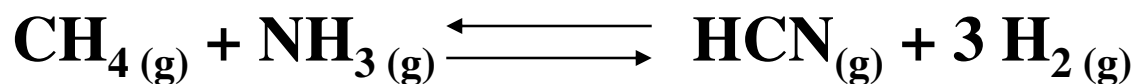


Forces the reaction equilibrium to go back to the left and produce more of the reactants.

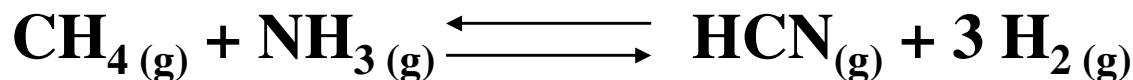
The Effect of a Change in Concentration–II



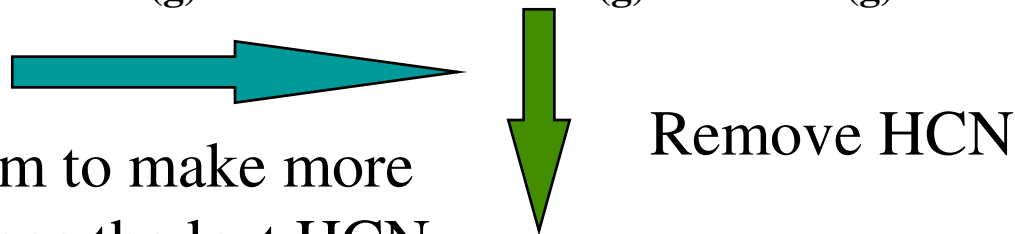
If to this same equilibrium mixture one decides to add one of the products to the equilibrium mixture, it will force the equilibrium back toward the reactant side and increase the concentrations of reactants. Likewise, if one takes away some of the hydrogen or hydrogen cyanide from the product side, it will force the equilibrium to replace it.



Forces equilibrium to go
toward the reactant direction.



Forces equilibrium to make more
produce and replace the lost HCN.



The Effect of a Change in Concentration

- If a gaseous reactant or product is **added** to a system at equilibrium, the system will shift in a direction to **reduce the concentration of the added component**.
- If a gaseous reactant or product is **removed** from a system at equilibrium, the system will shift in a direction to **increase the concentration of the removed component**.

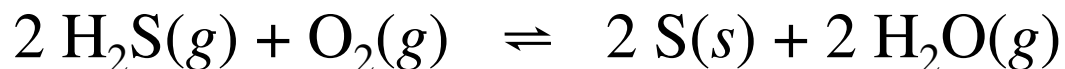


$$k_1 [\text{NO}_2]^2 = k_{-1} [\text{NO}][\text{NO}_3]$$

$$\frac{k_1}{k_{-1}} = \frac{[\text{NO}][\text{NO}_3]}{[\text{NO}_2]^2} = K$$

Examples: The Effect of a Change in Concentration

Consider the following reaction:



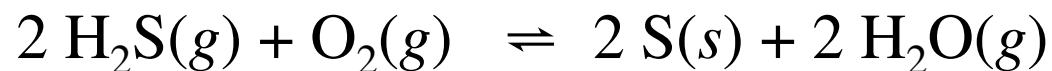
What happens to:

(a) $[\text{H}_2\text{O}]$ if O_2 is added?

The reaction proceeds to the right so H_2O increases.

(b) $[\text{H}_2\text{S}]$ if O_2 is added?

Some H_2S reacts with the added O_2 to move the reaction to the right, so $[\text{H}_2\text{S}]$ decreases.



(c) $[\text{O}_2]$ if H_2S is removed?

The reaction proceeds to the left to re-form H_2S , more O_2 is formed as well, O_2 increases.

(d) $[\text{H}_2\text{S}]$ if $\text{S}(s)$ is added?

S is a solid, so its activity does not change. Thus, $[\text{H}_2\text{S}]$ is unchanged.

The Effect of a Change in Pressure (Volume)

Pressure changes are mainly involving gases as liquids and solids are nearly incompressible. For gases, pressure changes can occur in three ways:

- Changing the concentration of a gaseous component
- Adding an inert gas (one that does not take part in the reaction)
- Changing the volume of the reaction vessel

When a system at equilibrium that contains a gas undergoes a change in pressure as a result of a change in volume, the equilibrium position shifts to reduce the effect of the change.

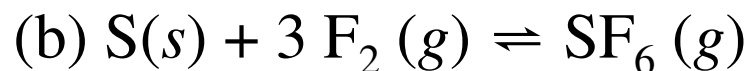
- If the volume is lower (pressure is higher), the total number of gas molecules decrease.
- If the volume is higher (pressure is lower), the total number of gas molecules increases.

Examples: The Effect of a Change in Pressure

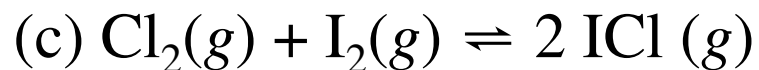
How would you change the total pressure or volume in the following reactions to increase the yield of the products:



The only gas is the product CO_2 . To move the reaction to the right increase the volume.



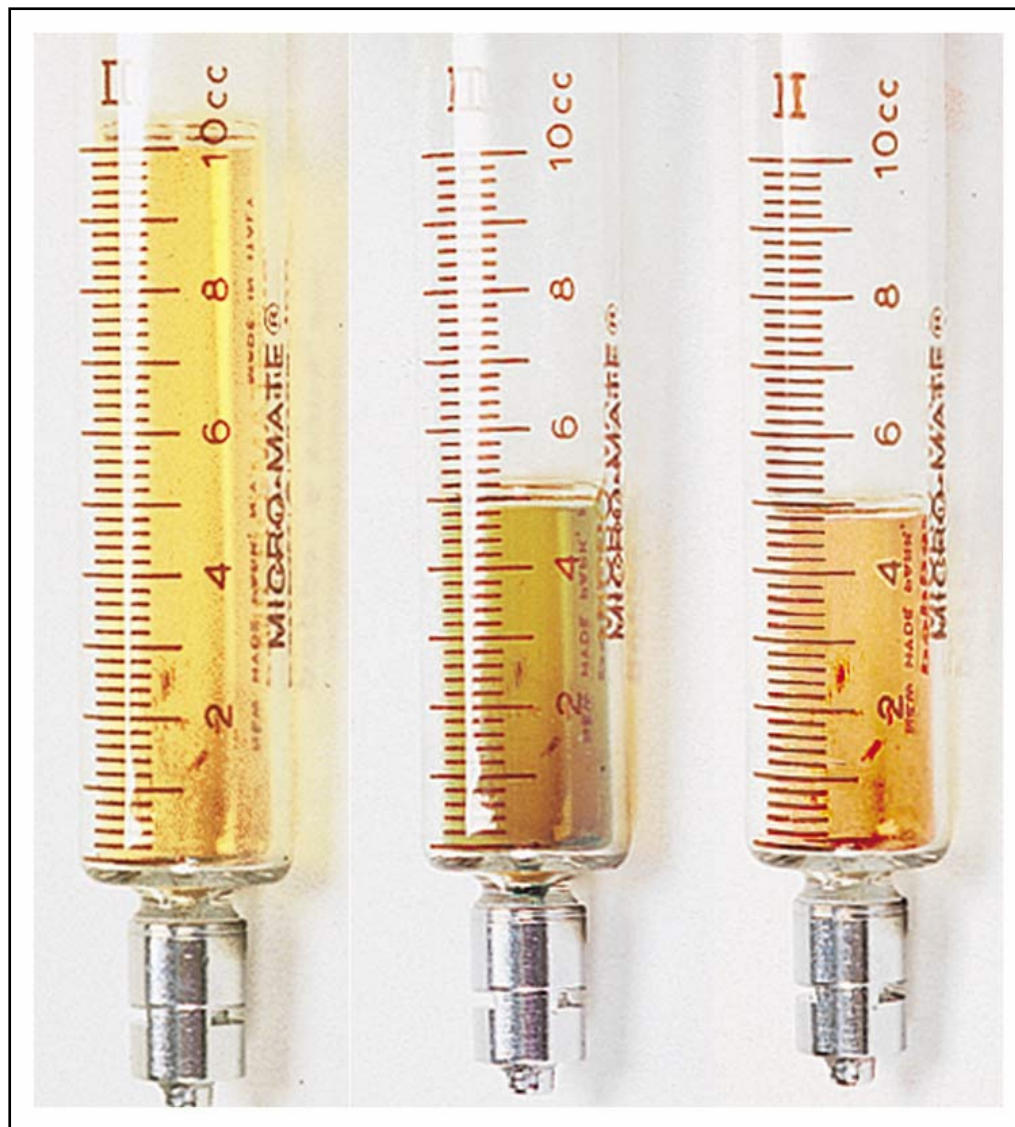
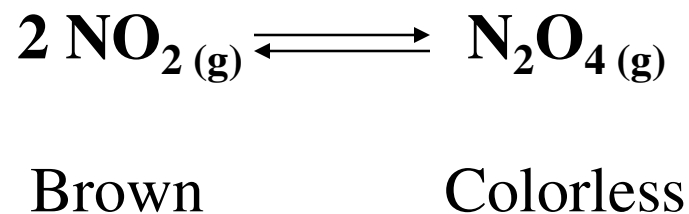
With 3 moles of gas on the left and only one on the right, we increase the pressure to form more SF_6 .



The number of moles of gas is the same on both sides of the equation, so a change in pressure or volume will have no effect.

Effect of Pressure on Nitrogen Oxide Equilibrium

Figure 6.9: Brown $\text{NO}_2(\text{g})$ and colorless $\text{N}_2\text{O}_4(\text{g})$ at equilibrium in a syringe

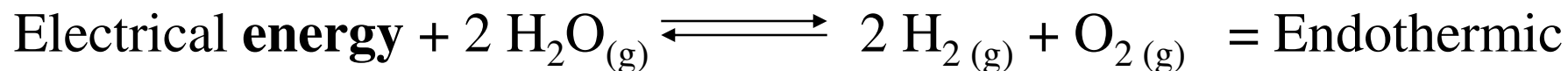
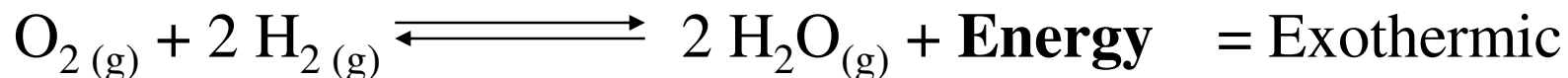


Source: Ken O'Donoghue

The Effect of a Change in Temperature

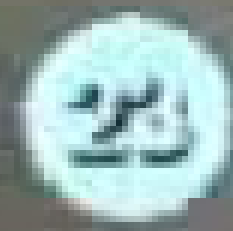
Only temperature changes will alter the equilibrium constant, and that is why we always specify the temperature when giving the value of K_c .

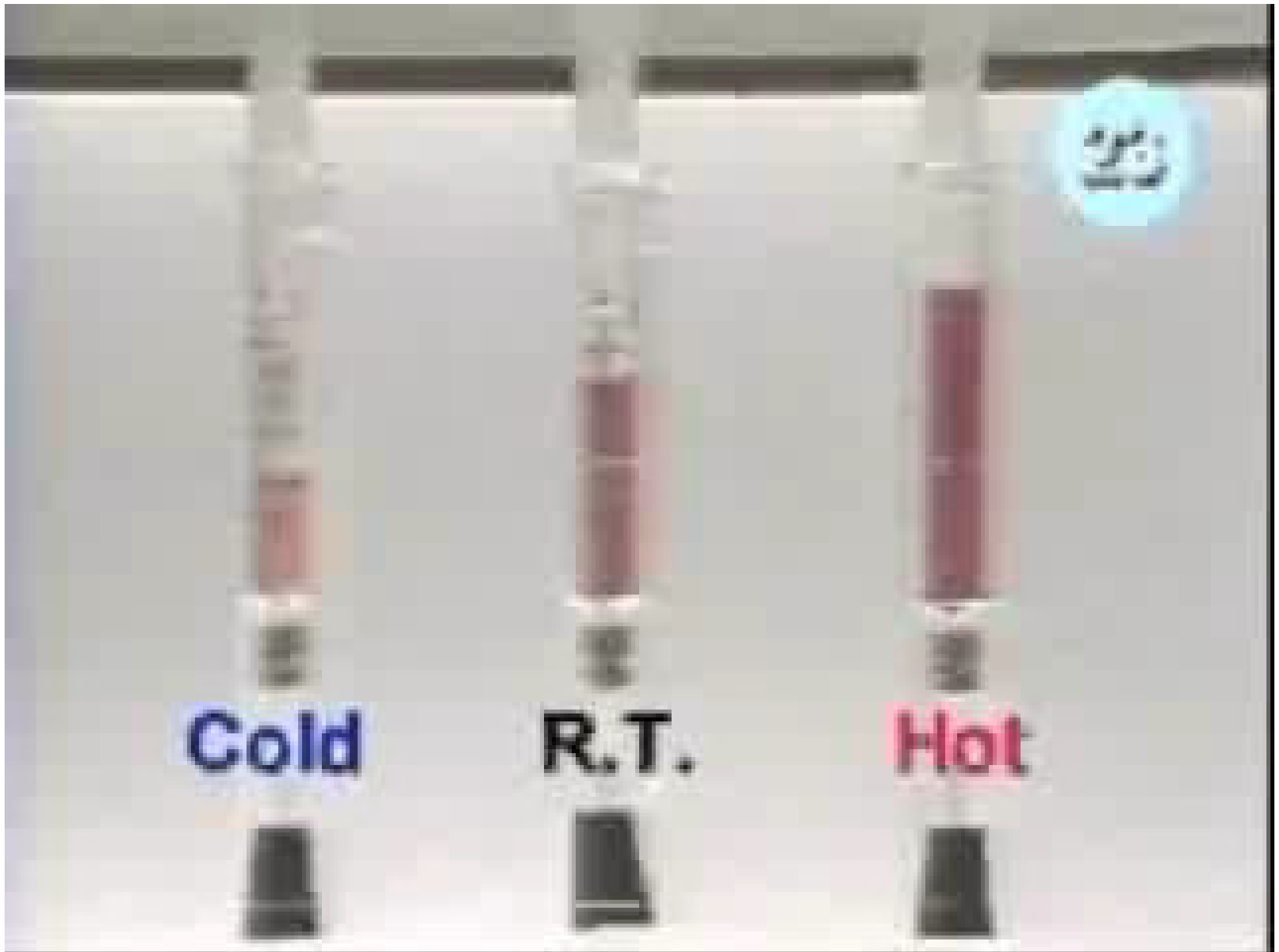
The best way to look at temperature effects is to realize that energy is a component of the equation, the same as a reactant, or product. For example, if you have an exothermic reaction, heat (energy) is on the product side of the equation, but if it is an endothermic reaction, it will be on the reactant side of the equation.



- A temperature increase favors the endothermic direction.
- A temperature decrease favors the exothermic direction.

Gaseous Equilibrium

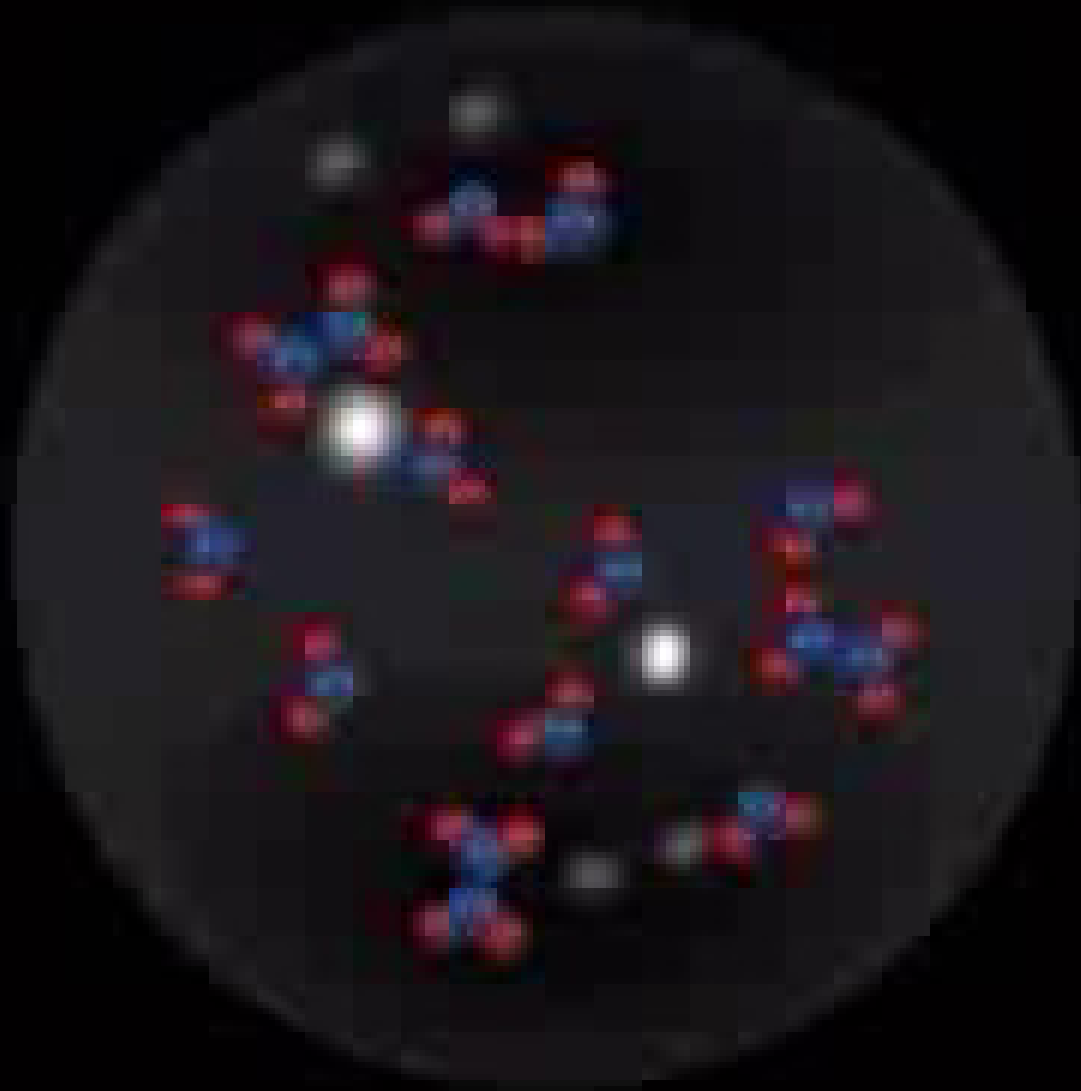




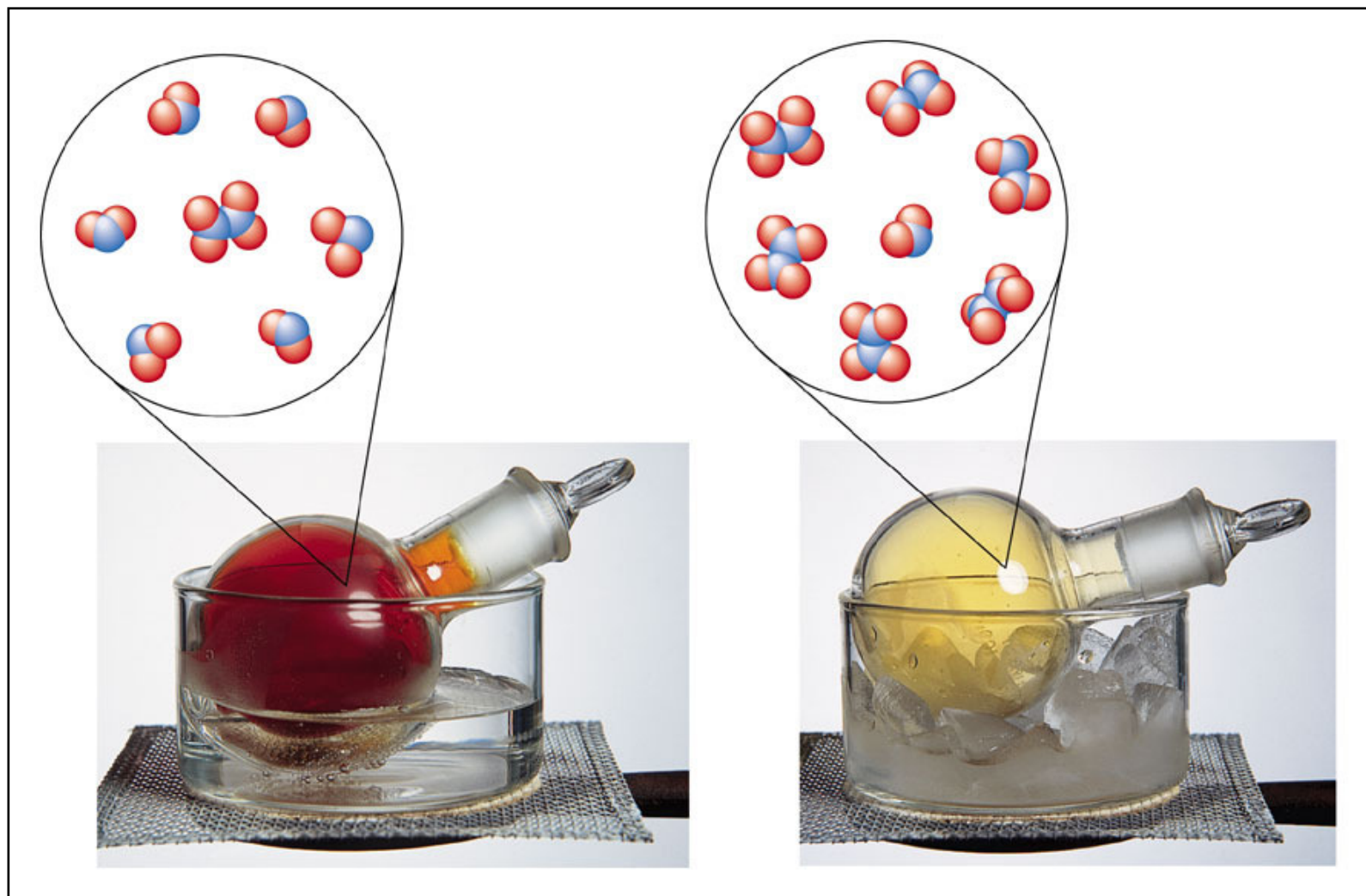
Cold

R.T.

Hot



Shifting the $\text{N}_2\text{O}_4(\text{g})$ and $2\text{NO}_2(\text{g})$ equilibrium by changing the temperature



Exothermic Reactions

- Release energy upon reaction. **Treat energy as a reaction product.** Use Le Chatelier's principle.
- Increasing T adds energy to system. The equilibrium shifts towards the reactants. (System absorbs energy)
- The value of K decreases in consequence.
- **Note that change in concentration at constant T changes equilibrium position, but not value of K.**

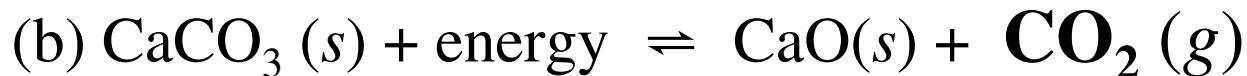
Endothermic Reactions

- Absorb energy upon reaction. **Treat energy as a reactant.** Use Le Chatelier's principle.
- Increasing T adds energy to system. The equilibrium shifts towards the products. (System absorbs energy)
- The value of K increases in consequence.

Example: How does an increase in temperature affect the equilibrium concentration of the **indicated** substance and K for the following reactions:



Increasing T adds thermal energy. This shifts the system to the left, where it absorbs energy. $[\text{Ca}(\text{OH})_2]$ and K decrease.



Increasing T adds thermal energy. This shifts the system to the right, where it absorbs energy. $[\text{CO}_2]$ and K increase.

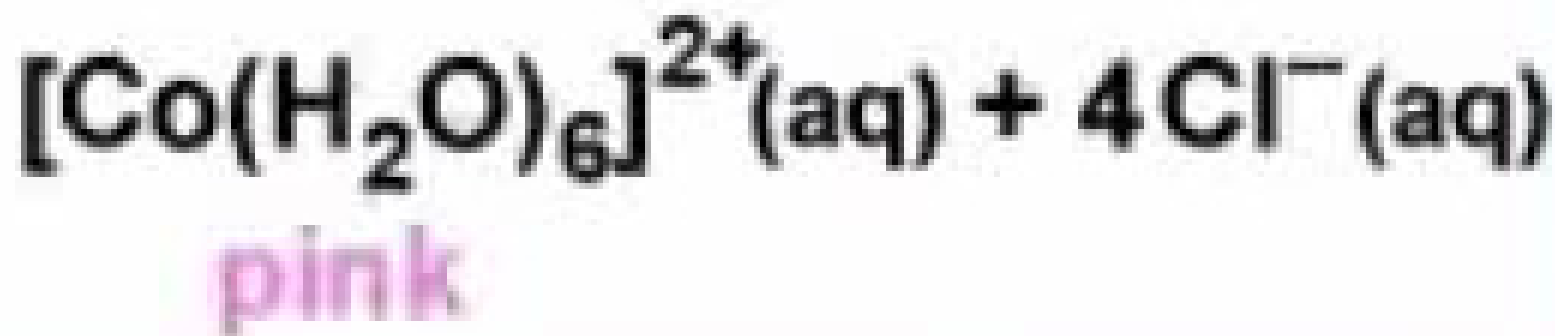
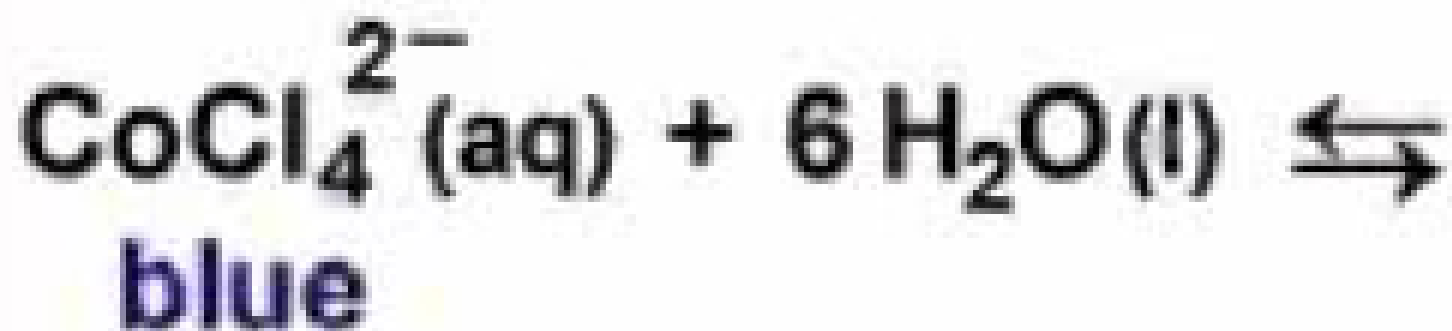


Increasing T adds thermal energy. This shifts the system to the right, where it absorbs energy. $[\text{SO}_2]$ will decrease and K increases.

Effect of Various Stresses on an Equilibrium System

Stress	Net Direction of Reaction	Effect on Value of K
<i>Concentration</i>		
Increase [reactant]	Toward formation of products	None
Decrease [reactant]	Toward formation of reactants	None
<i>Volume (of closed container holding reaction at constant T)</i>		
Increase V	Toward formation of larger amount (mol) of gas unless $\Delta n = 0$	None
Decrease V	Toward formation of smaller amount (mol) of gas unless $\Delta n = 0$	None
<i>Temperature - Adding energy in form of heat (Opposite if T decrease...):</i>		
Increase T	Toward formation of products if energy is a “reactant” (endothermic reaction)	K increases with T increase
	Toward formation of reactants if energy is a “product” (exothermic reaction)	K decreases with T increase

The equilibrium we are going to consider is:





$$Q = \frac{[\text{Co}(\text{H}_2\text{O})_6^{2+}][\text{Cl}^{-}]^4}{[\text{CoCl}_4^{2-}]}, \text{ which initially } = K$$

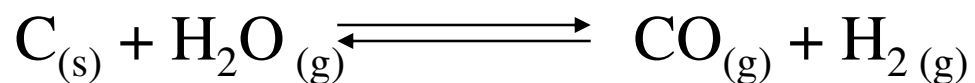
DEMO!

Ways of Expressing the Reaction Quotient, Q , and K

Form of Chemical Equation	Form of Q	Value of K
Reference reaction: $A \rightleftharpoons B$	$Q_{(\text{ref})} = \frac{[B]}{[A]}$	$K_{(\text{ref})} = \frac{[B]_{\text{eq}}}{[A]_{\text{eq}}}$
Reverse reaction: $B \rightleftharpoons A$	$Q = \frac{1}{Q_{(\text{ref})}} = \frac{[A]}{[B]}$	$K = \frac{1}{K_{(\text{ref})}}$
Reaction as sum of two steps: (1) $A \rightleftharpoons C$ (2) $C \rightleftharpoons B$ ----- Net: $A \rightleftharpoons B$	$Q_1 = \frac{[C]}{[A]}$; $Q_2 = \frac{[B]}{[C]}$ $Q_{\text{overall}} = Q_1 \times Q_2 = Q_{(\text{ref})}$ $= \frac{[C]}{[A]} \times \frac{[B]}{[C]} = \frac{[B]}{[A]} = Q_{(\text{ref})}$ or $K_{(\text{ref})}$	$K_{\text{overall}} = K_1 \times K_2$
Coefficients multiplied by n :	$Q = Q_{(\text{ref})}^n$	$K = K_{(\text{ref})}^n$
Reaction with pure solid or liquid component, such as $A_{(s)}$:	Replace that [] with 1	

Predicting the Effect of a Change in Concentration on the Position of the Equilibrium

Problem: Carbon will react with water to yield carbon monoxide and hydrogen, in a reaction called the water gas reaction that was used to convert coal into a fuel that can be used by industry.



What happens to:

(a) [CO] if C is added?

(c) [H₂O] if H₂ is added?

(b) [CO] if H₂O is added?

(d) [H₂O] if CO is removed?

Plan: We either write the reaction quotient to see how equilibrium will be effected, or look at the equation, and predict the change in direction of the reaction, and the effect of the material desired.

Solution: (a) No change, as carbon is a solid, and not involved in the equilibrium, as long as some carbon is present to allow the reaction.

(b) The reaction moves to the product side, and [CO] increases.

(c) The reaction moves to the reactant side, and [H₂O] increases.

(d) The reaction moves to the product side, and [H₂O] decreases.