

Chapter 15: Chemical Equilibrium

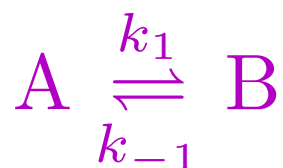
Key topics:

Equilibrium Constant

Calculating Equilibrium Concentrations

The Concept of Equilibrium

Consider the reaction



At equilibrium there is no net change in [A] or [B], namely

$$\frac{d[A]}{dt} = 0 = \frac{d[B]}{dt}$$

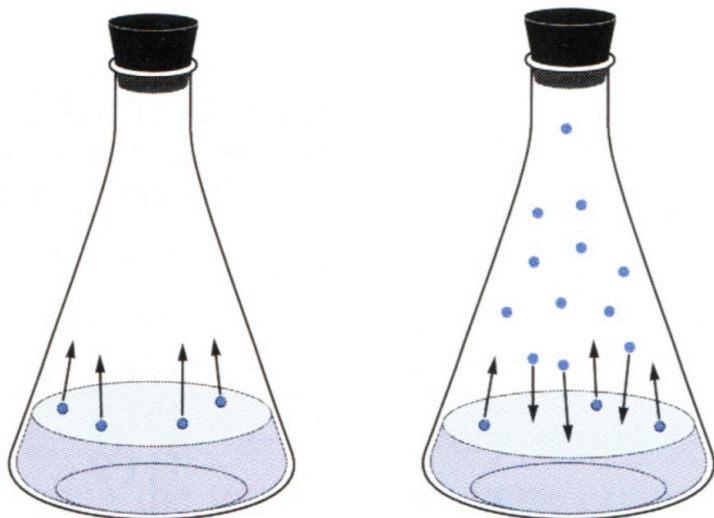
But A molecules can react to form B, and B molecules can react to form A, if the forwards and backwards rates are equal.

$$k_1[A] = k_{-1}[B]$$

This is because

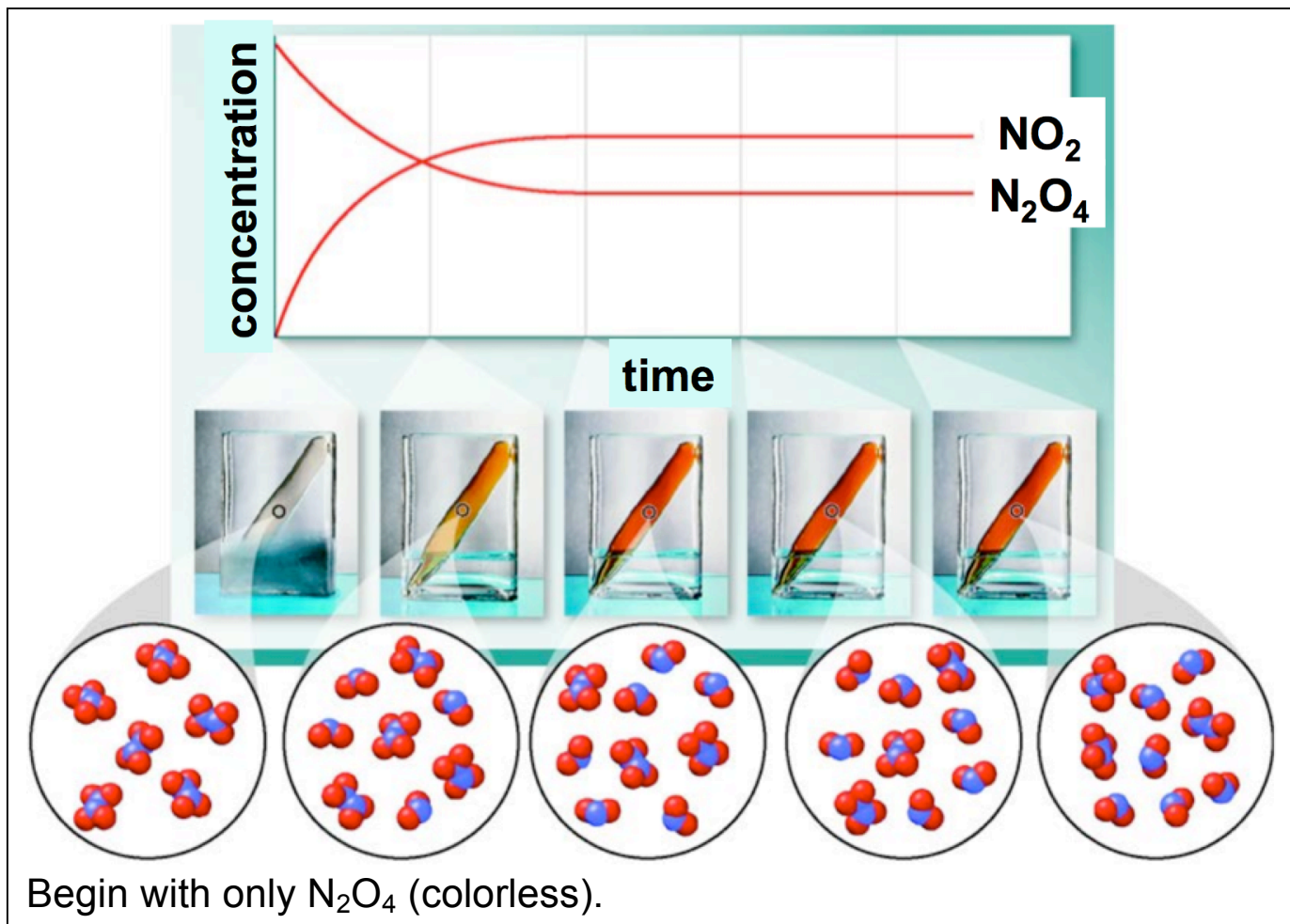
$$\frac{d[A]}{dt} = -k_1[A] + k_{-1}[B]$$

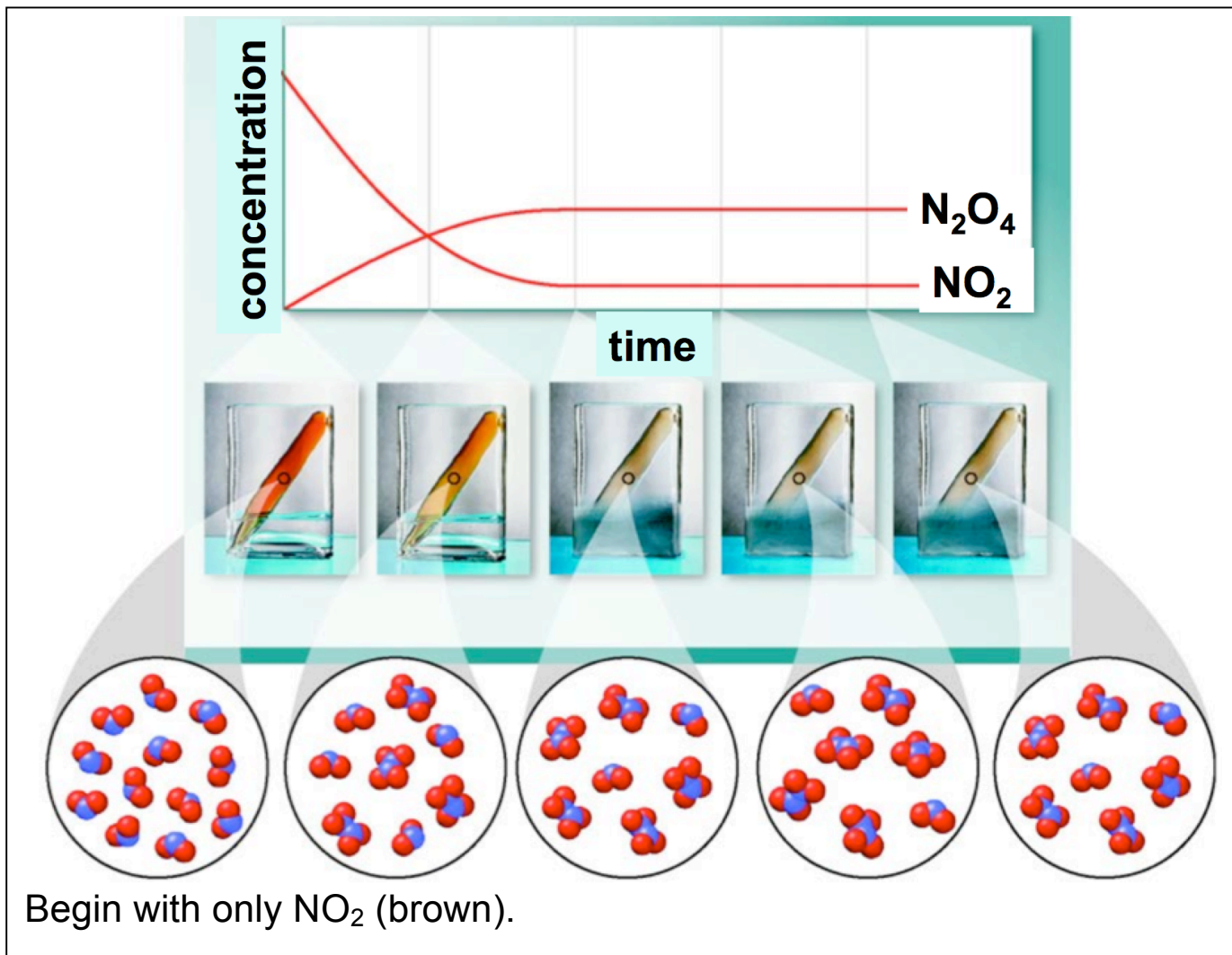
At the molecular level, typically the reactions do not stop.



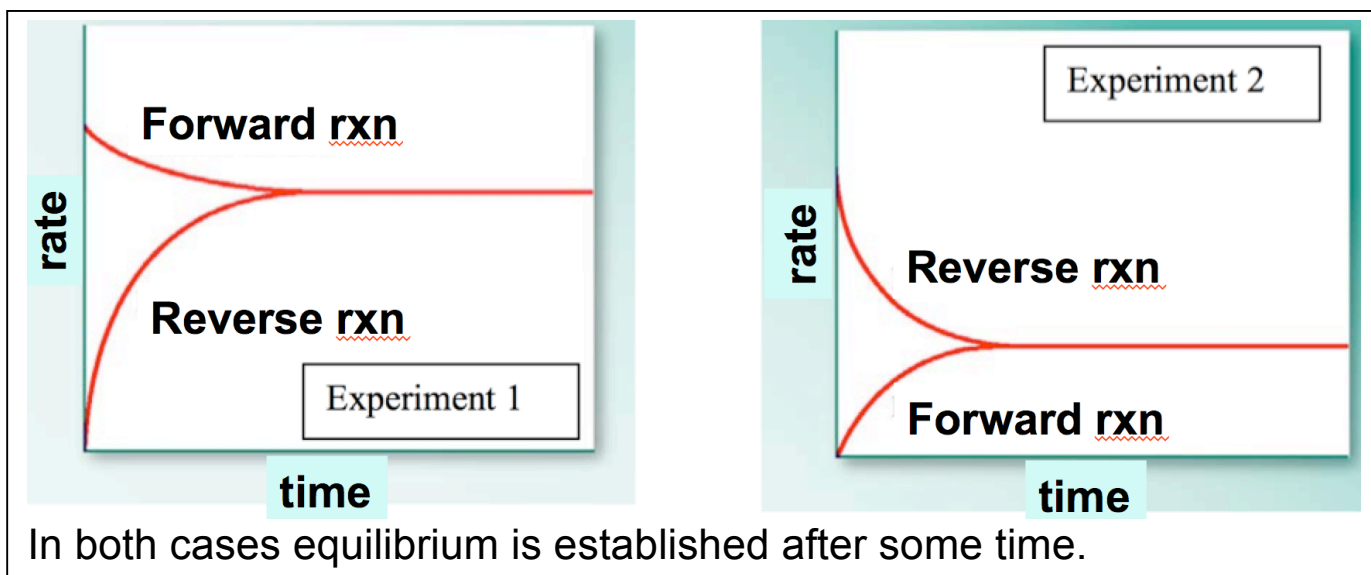
Initially there is net evaporation of liquid, but after dynamic equilibrium is established, the rate of evaporation = rate of condensation. (from chemtutorial.net)

Consider the reaction $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$





The forward rate = $k_f[N_2O_4]$; the reverse rate = $k_r[NO_2]^2$
 (the elementary reactions are the same as the overall reaction)



The Equilibrium Constant

At equilibrium the forwards and reverse rates are equal

$$k_f[\text{N}_2\text{O}_4]_{eq} = k_r[\text{NO}_2]_{eq}^2 \Rightarrow \frac{k_f}{k_r} = \frac{[\text{NO}_2]_{eq}^2}{[\text{N}_2\text{O}_4]_{eq}} = K_c$$

K_c is the equilibrium constant (the “c” here stands for concentration).

In general, to write an equilibrium constant

- products over reactants
- exponents are the coefficients from the balanced reaction

TABLE 15.1

Initial and Equilibrium Concentrations of N_2O_4 and NO_2 at 25°C

Experiment	Initial Concentrations (M)		Equilibrium Concentrations (M)		
	$[\text{N}_2\text{O}_4]_i$	$[\text{NO}_2]_i$	$[\text{N}_2\text{O}_4]_{eq}$	$[\text{NO}_2]_{eq}$	$\frac{[\text{NO}_2]_{eq}^2}{[\text{N}_2\text{O}_4]_{eq}}$
1	0.670	0.00	0.643	0.0547	4.65×10^{-3}
2	0.446	0.0500	0.448	0.0457	4.66×10^{-3}
3	0.500	0.0300	0.491	0.0475	4.60×10^{-3}
4	0.600	0.0400	0.594	0.0523	4.60×10^{-3}
5	0.000	0.200	0.0898	0.0204	4.63×10^{-3}

Magnitude of the Equilibrium Constant

- If $K_c \gg 1$, products are favored (rxn nearly complete).
- If $K_c \ll 1$, reactants are favored (rxn hardly proceeds).
- If K_c is close to 1, the system contains comparable amounts of products and reactants.

The **reaction quotient** Q_c is the same expression but without necessarily being at equilibrium.

In general, for $aA + bB \rightleftharpoons cC + dD$,

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

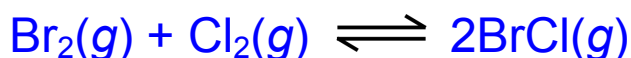
The Q_c expression is also called the law of mass action.

e.g., Write the reaction quotient for
 $\text{Cd}^{2+}(\text{aq}) + 4\text{Br}^{-}(\text{aq}) \rightleftharpoons \text{CdBr}_4^{2-}(\text{aq})$

Solution:

$$Q_c = \frac{[\text{CdBr}_4^{2-}]}{[\text{Cd}^{2+}][\text{Br}^{-}]^4}$$

e.g., In an analysis of the following reaction at 100°C



the equilibrium concentrations are $[\text{Br}_2] = 2.3 \times 10^{-3} \text{ M}$,
 $[\text{Cl}_2] = 1.2 \times 10^{-2} \text{ M}$, $[\text{BrCl}] = 1.4 \times 10^{-2} \text{ M}$. Write the equilibrium expression and calculate K_c for this reaction.

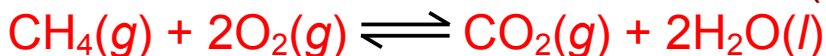
Solution:

$$K_c = \frac{[\text{BrCl}]^2}{[\text{Br}_2][\text{Cl}_2]} = \frac{(1.4 \times 10^{-2})^2}{(2.3 \times 10^{-3})(1.2 \times 10^{-2})} = 7.1$$

Equilibrium Expressions

So far we have looked at **homogeneous equilibria**, in which all the reactants and products are in the same phase.

For **heterogeneous equilibria**, there is an additional factor: Consider the combustion of methane (natural gas):



If we proceed as before, we would have

$$K_c^* = \frac{[\text{CO}_2][\text{H}_2\text{O}]^2}{[\text{CH}_4][\text{O}_2]^2}$$

But $[\text{H}_2\text{O}]$ is a constant: The concentration of water is always

$$\frac{1 \text{ g}}{\text{mL}} \cdot \frac{1000 \text{ mL}}{1 \text{ L}} \cdot \frac{\text{mol}}{18 \text{ g}} = 55 \text{ mol/L}$$

So we define the equilibrium constant as $K_c = K_c^* [\text{H}_2\text{O}]^2$

We do this whenever there is a pure liquid or solid in the rxn.

e.g., Write the equilibrium expression for



Solution:

We include the solid in K, so

$$K_c = \frac{1}{[\text{Hg}^{2+}][\text{Cl}^-]^2}$$

e.g., Does the following equilibrium expression correspond to homogeneous or heterogeneous equilibrium?

$$K_c = \frac{[\text{Ag}(\text{NH}_3)_2^+][\text{Cl}^-]}{[\text{NH}_3]^2}$$

Solution:

The reactants are supposed to be on the bottom and the products on top; clearly we are missing AgCl from the reactants, which is insoluble (solid phase).

Manipulating Equilibrium Expressions

1. Reversing the direction of a reaction:



$$K_c = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} \quad \text{vs.} \quad K'_c = \frac{[\text{N}_2\text{O}_4]}{[\text{NO}_2]^2}$$

Clearly $K'_c = \frac{1}{K_c}$

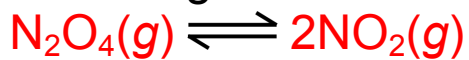
2. Coefficient changes



$$K_c = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} \quad \text{vs.} \quad K'_c = \frac{[\text{NO}_2]^4}{[\text{N}_2\text{O}_4]^2}$$

Clearly $K'_c = K_c^2$

3. Adding chemical reactions together



$$K_{c_1} = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]}$$



$$K_{c_2} = \frac{[\text{NO}]^2[\text{O}_2]}{[\text{NO}_2]^2}$$



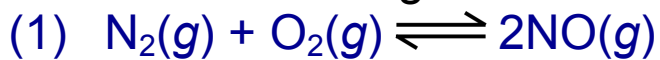
$$K_c = \frac{[\text{NO}]^2[\text{O}_2]}{[\text{N}_2\text{O}_4]}$$

Clearly $K_c = K_{c_1} \times K_{c_2}$

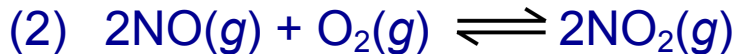
TABLE 15.2 Manipulation of Equilibrium Constant Expressions			
	$\text{A}(\text{g}) + \text{B}(\text{g}) \rightleftharpoons 2\text{C}(\text{g})$	$K_{c_1} = 4.39 \times 10^{-3}$	
	$2\text{C}(\text{g}) \rightleftharpoons \text{D}(\text{g}) + \text{E}(\text{g})$	$K_{c_2} = 1.15 \times 10^4$	
Equation	Equilibrium Expression	Relationship to Original K_c	Equilibrium Constant
$2\text{C}(\text{g}) \rightleftharpoons \text{A}(\text{g}) + \text{B}(\text{g})$ Original equation is reversed.	$K'_{c_1} = \frac{[\text{A}]_{\text{eq}}[\text{B}]_{\text{eq}}}{[\text{C}]_{\text{eq}}^2}$	$\frac{1}{K_{c_1}}$	2.28×10^2 New constant is the reciprocal of the original.
$2\text{A}(\text{g}) + 2\text{B}(\text{g}) \rightleftharpoons 4\text{C}(\text{g})$ Original equation is multiplied by a number.	$K''_{c_1} = \frac{[\text{C}]_{\text{eq}}^4}{[\text{A}]_{\text{eq}}^2[\text{B}]_{\text{eq}}^2}$	$(K_{c_1})^2$	1.93×10^{-5} New constant is the original raised to the same number.
$\frac{1}{2}\text{A}(\text{g}) + \frac{1}{2}\text{B}(\text{g}) \rightleftharpoons \text{C}(\text{g})$ Original equation is divided by 2.	$K'''_{c_1} = \frac{[\text{C}]_{\text{eq}}}{[\text{A}]_{\text{eq}}^{1/2}[\text{B}]_{\text{eq}}^{1/2}}$	$\sqrt{K_{c_1}}$	6.63×10^{-2} New constant is the square root of the original.
$\text{A}(\text{g}) + \text{B}(\text{g}) \rightleftharpoons \text{D}(\text{g}) + \text{E}(\text{g})$ Two equations are added.	$K_{c_3} = \frac{[\text{D}]_{\text{eq}}[\text{E}]_{\text{eq}}}{[\text{A}]_{\text{eq}}[\text{B}]_{\text{eq}}}$	$K_{c_1} \times K_{c_2}$	50.5 New constant is the product of the two original constants.

*Temperature is the same for both reactions.

e.g., Given the following data:

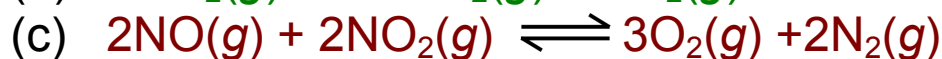
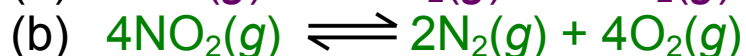
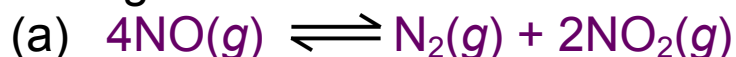


$$K_{c1} = 4.3 \times 10^{-25}$$



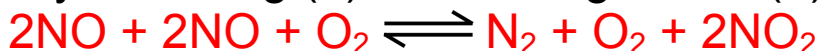
$$K_{c2} = 6.4 \times 10^9$$

Determine the values of the equilibrium constants for the following reactions:



Solution:

(a) Try reversing (1) and adding this to (2):



This is what we want and thus $K_c = (1/K_{c1})(K_{c2}) = 1.5 \times 10^{34}$

(b) Try reversing both (1) and (2), and add them:



Then we can double this to get what we want, which gives $K_c = [(1/K_{c1})(1/K_{c2})]^2 = (3.6 \times 10^{14})^2 = 1.3 \times 10^{29}$

(c) Try reversing both $2 \times (1)$ and (2), and add them:



which gives $K_c = (1/K_{c1})^2 (1/K_{c2}) = 8.5 \times 10^{38}$

Gaseous Equilibria

For reactions involving only gases, we can use partial pressures instead of concentrations to express the equilibrium:

Consider $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$

$$K_c = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} \quad K_P = \frac{[P_{\text{NO}_2}]^2}{[P_{\text{N}_2\text{O}_4}]}$$

Here the “c” stands for concentration; “P” stands for pressure.

There is a straightforward relationship between K_c and K_P :
From the ideal gas law, applied to an arbitrary species “A”

$$PV = nRT \Rightarrow P_A = \frac{n_A}{V} RT = [A]RT$$

Therefore for $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$,

$$K_P = \frac{[P_{\text{NO}_2}]^2}{[P_{\text{N}_2\text{O}_4}]} = \frac{[\text{NO}_2]^2 (RT)^2}{[\text{N}_2\text{O}_4] (RT)} = K_c (RT)$$

In general,

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

where Δn = moles of products – moles of reactants.

e.g., For the reaction $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$

$K_c = 2.3 \times 10^{-2}$ at 375°C . Calculate K_P at this temperature.

Solution:

$$K_P = K_c (RT)^{\Delta n} \text{ and here } \Delta n = 2 - (1 + 3) = 2 - 4 = -2.$$

$$K_P = 2.3 \times 10^{-2} [0.08206 \times (375 + 273)]^{-2} = 8.1 \times 10^{-6}$$

Using Q and K to Predict the Direction of a Reaction

We can predict the direction of a reaction by comparing the values of Q and K.

$Q > K \Rightarrow$ reverse reaction favored

$Q = K \Rightarrow$ equilibrium present

$Q < K \Rightarrow$ forward reaction favored

e.g., At 448°C, $K_P = 51$ for $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$
Predict the direction the reaction will proceed, if at 448°C the pressures of HI, H₂, and I₂ are 1.3, 2.1, and 1.7 atm.

Solution:

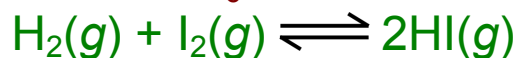
The reaction quotient is
$$Q_P = \frac{P_{\text{HI}}^2}{P_{\text{H}_2} P_{\text{I}_2}} = \frac{(1.3)^2}{(2.1)(1.7)} = 0.47$$
so the reaction will proceed in the forward direction.

Calculating Equilibrium Concentrations

Method for calculating equilibrium concentrations from K_c and initial concentrations:

1. Construct an equilibrium table (**ICE table**), and fill in the initial concentrations (including any that are zero)
2. Use initial concentrations to calculate the reaction quotient, Q , and compare Q to K to determine the direction in which the reaction will proceed.
3. Define x as the amount of a particular species consumed, and use the stoichiometry of the reaction to define the amount of other species consumed or produced in terms of x .
4. For each species in the equilibrium, add the change in concentration to the initial concentration to get the equilibrium concentration.
5. Use the equilibrium concentrations and the equilibrium expression to solve for x .
6. Using the calculated value of x , determine the concentrations of all species at equilibrium.
7. Check your work by plugging the calculated equilibrium concentrations into the equilibrium expression. The result should be very close to the K_C stated in the problem.

e.g., Determine the initial concentration of HI if the initial concentrations of H_2 and I_2 are both 0.10 M and their equilibrium concentrations are both 0.043 M at 430°C . The value of $K_c = 54.3$



Solution:

	$\text{H}_2(\text{g})$	+	$\text{I}_2(\text{g})$	\rightleftharpoons	$2\text{HI}(\text{g})$
Initial	0.10		0.10		y
Change	-x		-x		+2x
Equilibrium	0.043		0.043		y + 2x

First solve for x: $0.10 - x = 0.043$; $x = 0.057$

Then solve for y: at equilibrium we have

$$K_c = 54.3 = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{(y + 0.114)^2}{(0.043)(0.043)}$$

$$(y + 0.114)^2 = (54.3)(0.043)^2 \Rightarrow y = \sqrt{(54.3)(0.043)^2} - 0.114 = 0.203$$

e.g., At 1280°C the equilibrium constant K_c for the reaction $\text{Br}_2(\text{g}) \rightleftharpoons 2\text{Br}(\text{g})$ is $K_c = 1.1 \times 10^{-3}$. If the initial concentrations are $[\text{Br}_2] = 6.3 \times 10^{-2}\text{ M}$ and $[\text{Br}] = 1.2 \times 10^{-2}\text{ M}$, calculate the equilibrium concentrations.

Solution:

First we should decide which way the reaction proceeds:

$$Q_c = \frac{[\text{Br}]^2}{[\text{Br}_2]} = \frac{(1.2 \times 10^{-2})^2}{6.3 \times 10^{-2}} = 2.3 \times 10^{-3}$$

Since $Q_c > K_c$, the reaction will go backwards

	$\text{Br}_2(\text{g})$	\rightleftharpoons	$2\text{Br}(\text{g})$
Initial	6.3×10^{-2}		1.2×10^{-2}
Change	+x (since backwards)		-2x
Equilibrium	$6.3 \times 10^{-2} + x$		$1.2 \times 10^{-2} - 2x$

The equilibrium expression is

$$K_c = \frac{[\text{Br}]^2}{[\text{Br}_2]} = \frac{(1.2 \times 10^{-2} - 2x)^2}{(6.3 \times 10^{-2} + x)}$$

$$\Rightarrow 1.44 \times 10^{-4} - 4.4x \times 10^{-2} + 4x^2 = K_c(6.3 \times 10^{-2} + x)$$

This is a quadratic equation in x . Let us rewrite it in the form

$$ax^2 + bx + c = 0 \quad \text{with}$$

$$a = 4$$

$$b = -4.4 \times 10^{-2} - 1.1 \times 10^{-3} = -4.51 \times 10^{-2}$$

$$c = 1.44 \times 10^{-4} - (1.1 \times 10^{-3})(6.3 \times 10^{-2}) = 7.47 \times 10^{-5}$$

Then we know the solution is (quadratic formula)

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

which yields

$$x = (0.0451 \pm 0.0290)/8 \Rightarrow x = 9.3 \times 10^{-3} \quad \text{or} \quad x = 2.0 \times 10^{-3}$$

With the first option, we get $[\text{Br}]_{\text{eq}} = 1.2 \times 10^{-2} - 2x = -6.6 \times 10^{-3}$

which is a negative number !! Therefore we know it must be the second option, finally giving

$$[\text{Br}]_{\text{eq}} = 8.0 \times 10^{-3} \text{ M and } [\text{Br}_2]_{\text{eq}} = 6.5 \times 10^{-2} \text{ M}$$

Comment: if we got the direction wrong at the start (if we predicted the reaction would go forwards) the quadratic equation gives $x = -9.3 \times 10^{-3}$ or $x = -2.0 \times 10^{-3}$ which, because of the minus signs, in fact tells us the reaction goes the other way (backwards). So we would still get the correct answer!

Sometimes we can simplify the expressions so that we don't have to use the quadratic formula.

e.g., $K_c = 3.39 \times 10^{-13}$ for $I_2(g) \rightleftharpoons 2I(g)$. Determine the equilibrium concentrations when a 1.00 L vessel originally charged with 0.00155 mol $I_2(g)$ is allowed to react.

Solution:

	$I_2(g)$	\rightleftharpoons	$2I(g)$
Initial	0.00155		0
Change	-x		+2x
Equilibrium	0.00155 - x		2x

$$K_c = \frac{[I]^2}{[I_2]} = \frac{(2x)^2}{0.00155 - x} \Rightarrow 4x^2 = K_c(0.00155 - x)$$

Since K_c is so small, we know very little I_2 reacts. Therefore we may assume that $(0.00155 - x) \approx 0.00155$

This gives

$$4x^2 = K_c(0.00155) = 5.25 \times 10^{-16} \Rightarrow x = 1.15 \times 10^{-8}$$

which, at equilibrium, gives $[I_2] = 0.00155$, $[I] = 2.3 \times 10^{-8} M$.

We can check that this agrees with K_c :

$$K_c = \frac{(2.3 \times 10^{-8})^2}{0.00155} = 3.4 \times 10^{-13}$$

which validates our assumption.

e.g., Consider a weak acid $\text{HA}(aq) \rightleftharpoons \text{H}^+(aq) + \text{A}^-(aq)$
 At 25°C, a 0.145 M solution of HA has $[\text{H}^+] = 2.2 \times 10^{-5} \text{ M}$.
 Determine K_c at 25°C.

Solution:

	$\text{HA}(aq) \rightleftharpoons$	$\text{H}^+(aq) +$	$\text{A}^-(aq)$
Initial	0.145	0	0
Change	-x	+x	+x
Equilibrium	0.145	2.2×10^{-5}	2.2×10^{-5}

$$K_c = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} = \frac{(2.2 \times 10^{-5})^2}{0.145} = 3.34 \times 10^{-9}$$

Le Chatelier's Principle: Factors that Affect Equilibrium

Le Chatelier's principle states that *if we do something to a system at equilibrium, the system will evolve to counteract us.*

Specifically, if we

- add a reactant or product
 - equilibrium will shift to remove it
- remove a reactant or product
 - equilibrium will shift to create it
- decrease the volume (increase the pressure)
 - equilibrium will shift to decrease the pressure
- increase the temperature for an endothermic reaction
 - reaction will go in the forward direction to cool down

However, there are a few aspects that are not so obvious, so we need to look at Le Chatelier's principle in more detail.

1. change [reactant] or [product] by adding/removing it:

This is best thought of in terms of Q versus K. **Before any change $Q = K$.** If Q changes by adding/removing reactant or product, then a net reaction will occur until $Q = K$ once again.

e.g., $K_c = 0.297$ for $\text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g)$

At equilibrium, $[\text{N}_2] = 2.05 \text{ M}$, $[\text{H}_2] = 1.56 \text{ M}$, $[\text{NH}_3] = 1.52 \text{ M}$.

Now we add $\text{N}_2(g)$ so that $[\text{N}_2] = 3.00 \text{ M}$. What happens?

$$Q_c = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} = \frac{(1.52)^2}{(3.00)(1.56)^3} = 0.203 < K_c$$

Therefore the reaction goes forwards (to remove N_2).

e.g., $2\text{H}_2\text{S}(g) + \text{O}_2(g) \rightleftharpoons 2\text{S}(s) + 2\text{H}_2\text{O}(g)$

If we remove elemental sulfur, $\text{S}(s)$, what happens?

This is a heterogeneous equilibrium expression, and therefore the solid phase species (sulfur) does not appear in Q or K.

There is no change.

2. change the volume in a reaction involving a gas:

Changing the volume changes the concentrations, and changes the partial pressures, of all gas species.

e.g., $K_c = 0.297$ for $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$

At equilibrium, $[\text{N}_2] = 2.05 \text{ M}$, $[\text{H}_2] = 1.56 \text{ M}$, $[\text{NH}_3] = 1.52 \text{ M}$.

Now we double the volume of the container. Therefore all the concentrations halve:

$$Q_c = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} = \frac{(1.52/2)^2}{(2.05/2)(1.56/2)^3} = 1.19 > K_c$$

Therefore the reaction goes backwards (to increase the number of moles of gas which increases the pressure)

e.g., $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$

This reaction does not respond to changes in volume.

3. add an inert gas at constant volume:

$K_c = 0.297$ for $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$

Now we add helium gas until the overall pressure has doubled.

What happens? Since we increased the pressure, you might think that the equilibrium will shift to lower the pressure, but this is not true. Why not?

Answer: there is no change in the concentrations of the reactions or products (also no change to the partial pressures). Therefore nothing happens.

4. change the temperature:

e.g., $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g}) \quad \Delta\text{H} = 58.0 \text{ kJ/mol}$ (endothermic)

We can write this as:

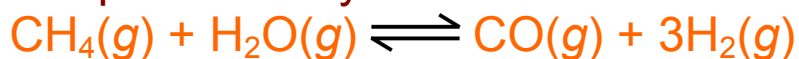


Then Le Chatelier's principle says that if we raise the temperature (add heat), the reaction will go forward to remove heat. Changing the temperature actually *changes* the value of the equilibrium constant (K_c depends on temperature).

5. add a catalyst:

A catalyst helps the system reach equilibrium *faster*, but it does not shift the equilibrium since it speeds up both the forwards and backwards directions equally.

e.g., Hydrogen is produced by the endothermic reaction



Assuming the reaction is initially at equilibrium, indicate the direction of the shift (left, right, or none) if

- $\text{H}_2\text{O}(\text{g})$ is removed
- The temperature is increased
- Nickel (Ni) catalyst is added
- An inert gas (He) is added
- The volume of the container is tripled