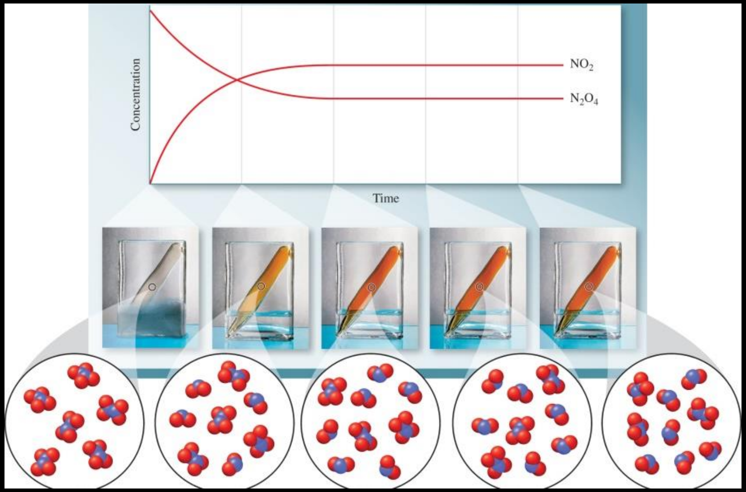
EQUILIBRIUM

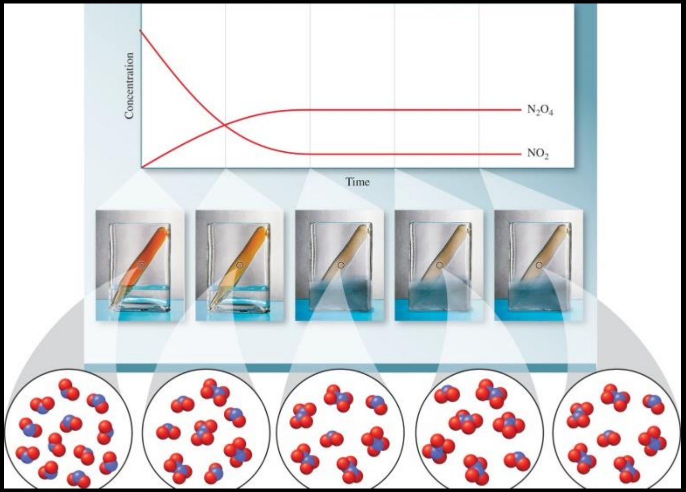
THE EQUILIBRIUM CONSTANT

THE EQUILIBRIUM CONSTANT K_C

At equilibrium, the forward rate equals the reverse rate of reaction.
For example:

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





THE EQUILIBRIUM CONSTANT K_C

This means, for this reaction, $k_f[N_2O_4]_{eq} = k_r[NO_2]^2_{eq}$ or

$$\frac{k_f}{k_r} = \frac{[\mathrm{NO_2}]^2_{eq}}{[\mathrm{N_2O_4}]_{eq}} = K_c$$

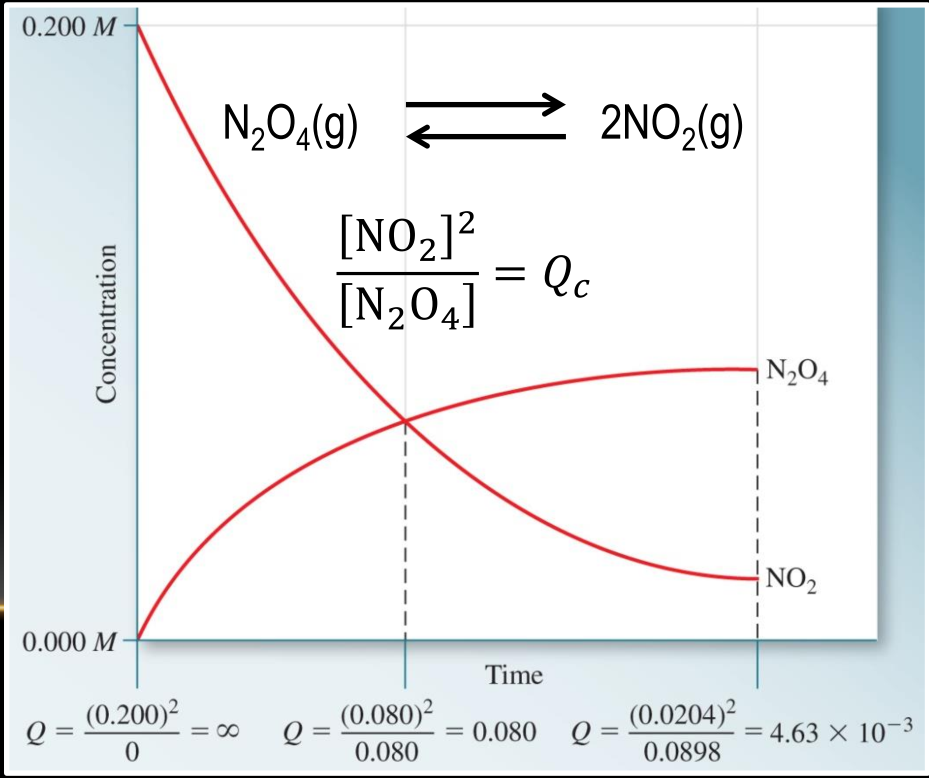
Here K_c is called the equilibrium constant. The subscript "c" stands for concentrations.

THE REACTION QUOTIENT, Q_C

For the general equation $aA + bB \rightleftharpoons cC + dD$

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

And at equilibrium, $K_c = Q_c$



EXTENT OF REACTION AND K_C

If stoichiometric amounts of the reactants are combined there are three possible scenarios:

1.) The reaction goes essentially to completion. K_c is large

2.) No significant reaction occurs. K_c is small

3.) The reaction occurs, but not to completion. The equilibrium mixture has appreciable amounts of reactants and products. K_c is usualy between 0.01 and 100.

EQUILIBRIUM EXPRESSIONS

HETEROGENEOUS EQUILIBRIA

Solids and liquids do not appear in the equilibrium expression because their concentration does not change.

Only aqueous species and gases appear in the equilibrium expression. Their concentrations do change.

For example: $2CaSO_4(s) \rightleftharpoons 2CaO(s) + 2SO_2(g) + O_2(g)$

$K_c = ?$

MANIPULATING EQUILIBRIUM EXPRESSIONS

When you reverse an equation, $K_R = 1/K_F$

When you multiply the coefficients of an equation by some number a, raise the K to that power: $K_{new} = K_{old}^{a}$

When you add equations, multiply their K's.

$$A(g) + B(g) \rightleftharpoons 2C(g) \qquad K_{c_1} = 4.39 \times 10^{-3}$$

$$2C(g) \rightleftharpoons D(g) + E(g) \qquad K_{c_2} = 1.15 \times 10^{4}$$

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

*Temperature is the same for both reactions.

GASEOUS EQUILIBRIA

For $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ $K_c = \frac{[\mathrm{NO_2}]^2}{[\mathrm{N_2O_4}]}$ and $K_P = \frac{(P_{NO_2})^2}{(P_{N_2O_4})}$

K_C is not usually equal to K_P because the molarity is not usually the same as the partial pressure of the gas.

The relationship between K_C and K_P is

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

Here R = 0.08206 L·atm/K ·mol, T is the temperature in K, and

Δn = moles of gaseous products – moles of gaseous reactants

EQUILIBRIUM CALCULATIONS

PREDICTING THE DIRECTION OF A REACTION

If $Q < K$, the ratio of concentrations of products to reactants is too small. The reaction proceeds to the right until equilibrium is achieved.

If $Q = K$ the reaction is at equilibrium. The is no shift in either direction.

If $Q > K$, the ratio of concentrations of products to reactants is too big. The reaction proceeds to the left until equilibrium is achieved.

EQUILIBRIUM CALCULATIONS

Knowing the equilibrium constant for a reaction, if we know the initial concentrations (or pressures) we can calculate the equilibrium concentrations (or pressures).

First, calculate Q to see which way the reaction proceeds.

Then set up an i.c.e. table.

For example, for the reaction

$$Br_2(g) \rightleftharpoons 2Br(g) \quad K_C = 1.1 \times 10^{-3} \text{ at } 1280\ ^oC$$

If the initial $[Br_2] = 6.3 \times 10^{-3}$ M and $[Br] = 1.2 \times 10^{-2}$ M, what are their equilibrium concentrations?

$[Br_2\ ] = 6.5 \times 10^{-2}$ M

$[Br] = 8.4 \times 10^{-3}$ M

LE CHÂTELIER'S PRINCIPLE

AFFECTING CHEMICAL EQUILIBRIUM

When a stress is applied to a system that is at equilibrium, the system will react in a manner so as to minimize the effect of the stress. To see what happens, look at Q.

Stress includes:

Changing the concentration or pressure of a reactant or product

Changing the volume or pressure of the system (this can change the concentrations and pressures)

Changing the temperature of the system

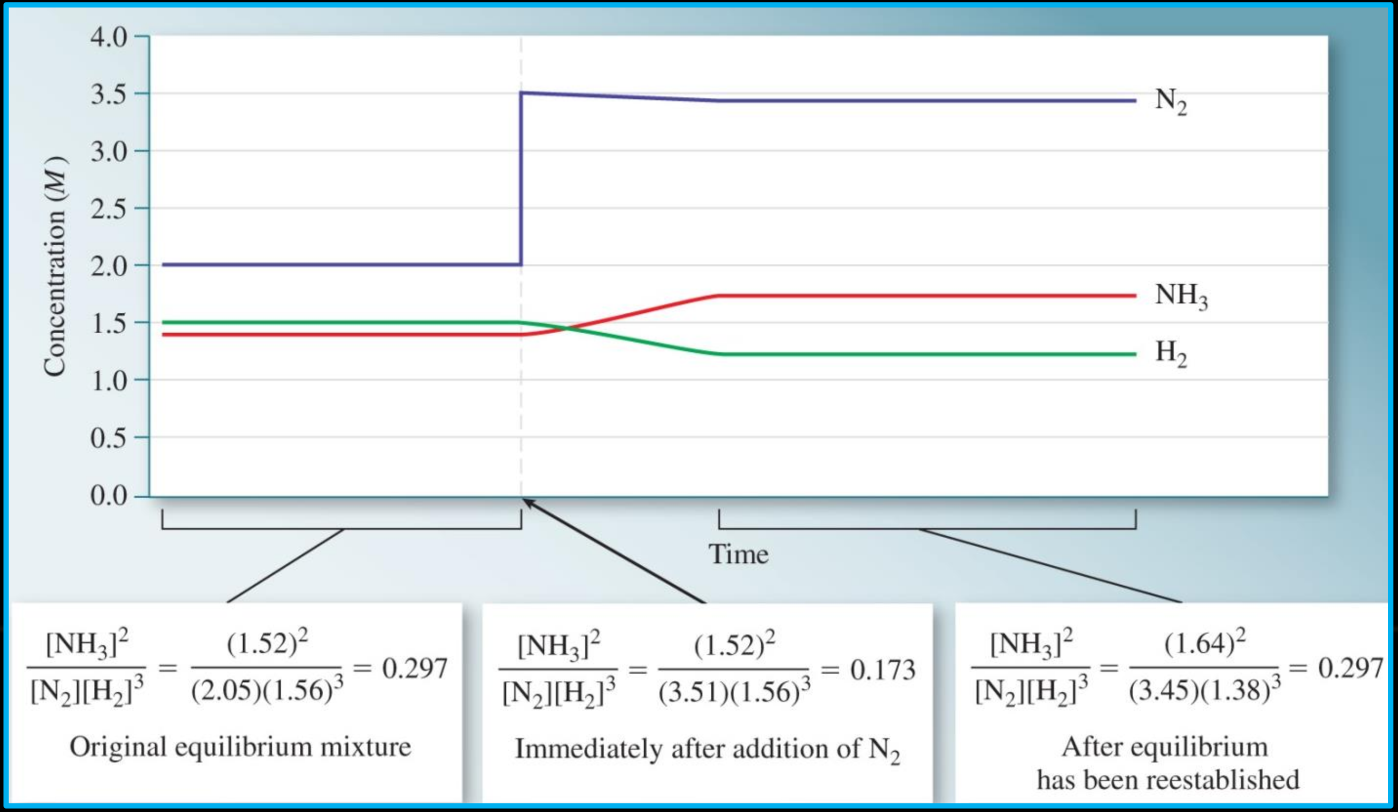
CHANGING CONCENTRATIONS

For the reaction:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

Look at what happens to Q_C when the equilibrium concentrations are disturbed.

$$K_C = 0.297$$



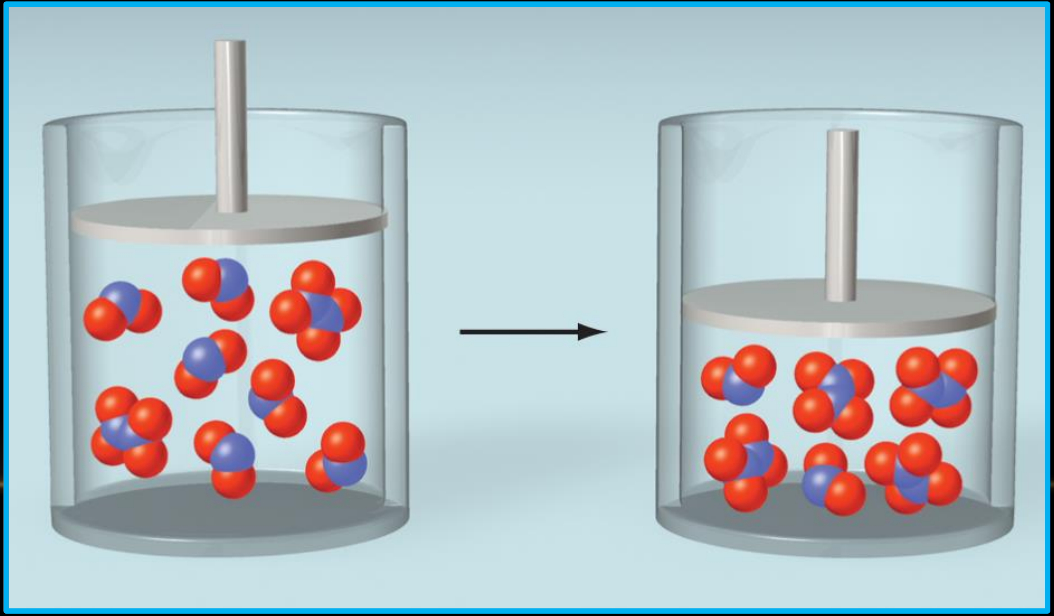
CHANGING VOLUME AND PRESSURE

For the following reaction:

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

$$K_C = 4.63 \times 10^{-3} \text{ at } 25\ ^oC.$$

If we start with $[NO_2]$ = 0.005199 M and $[N_2O_4]$ = 0.005838 M at equilibrium (and 25 ^{o}C) and decrease the volume in half (at constant temperature this doubles the total pressure). The concentrations are then initially doubled.

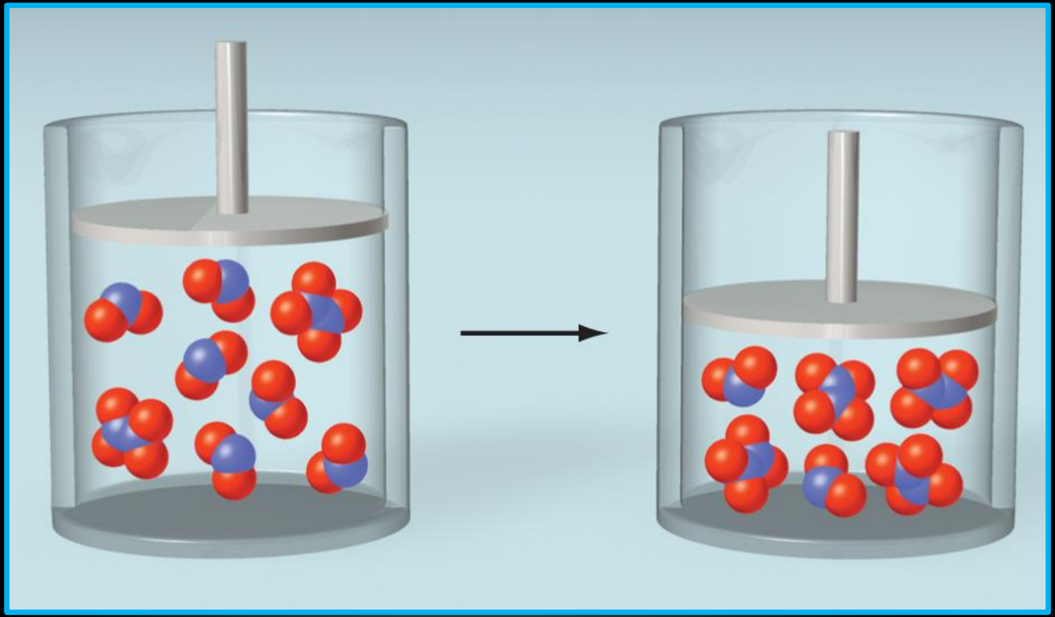


CHANGING VOLUME AND PRESSURE

$N_2O_4(g) \rightleftharpoons 2NO_2(g)$ $K_C = 4.63 \times 10^{-3}$ at 25 °C.

$$Q_C = \frac{(0.01039_8)^2}{0.01167_6} = 9.259_8 \times 10^{-3} > K_C$$

Equilibrium shifts to the left.



CHANGING VOLUME AND PRESSURE

In general, decreasing the volume (increasing the pressure) shifts the equilibrium to the side with fewer **gaseous** species.

In general, increasing the volume (decreasing the pressure) shifts the equilibrium to the side with more **gaseous** species.

CHANGING THE TEMPERATURE

Changes the value of K_C.

For an exothermic reaction (thermal energy is a product)

Increasing T shifts the equilibrium to the left

Decreasing T shifts the equilibrium to the right

For an endothermic reaction (thermal energy is a reactant)

Increasing T shifts the equilibrium to the right

Decreasing T shifts the equilibrium to the left

CATALYSTS

Affects neither K_C nor the the position of the equilibrium.

It does lower the activations energy, which increases the rate of the forward and reverse reactions equally.

If a system is not at equilibrium, a catalyst will allow the system to achieve equilibrium more rapidly.