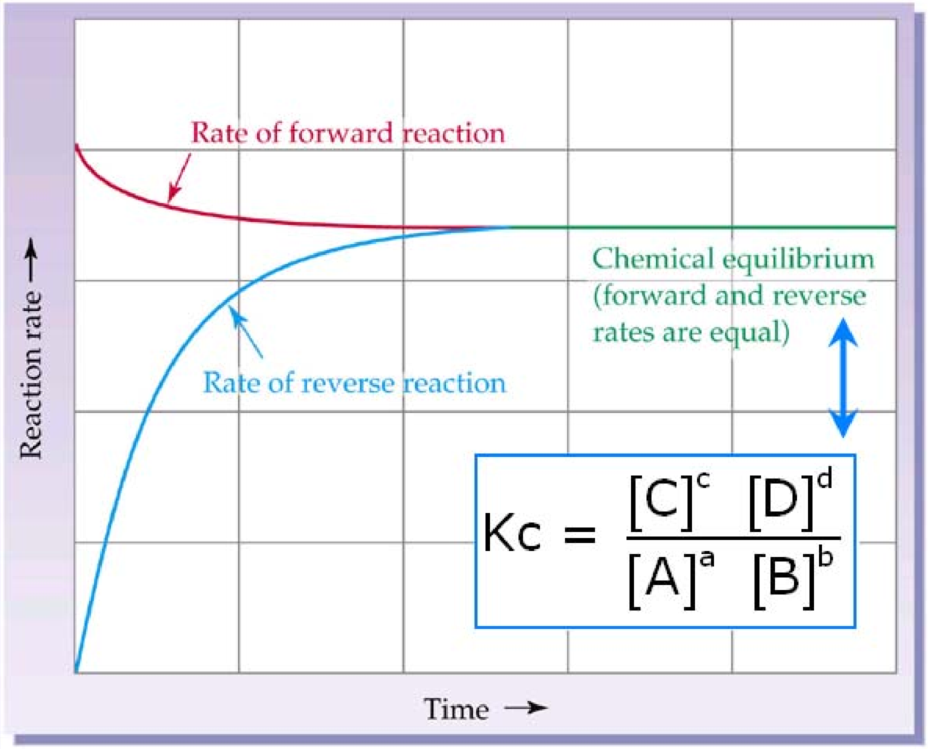
The equilibrium constant



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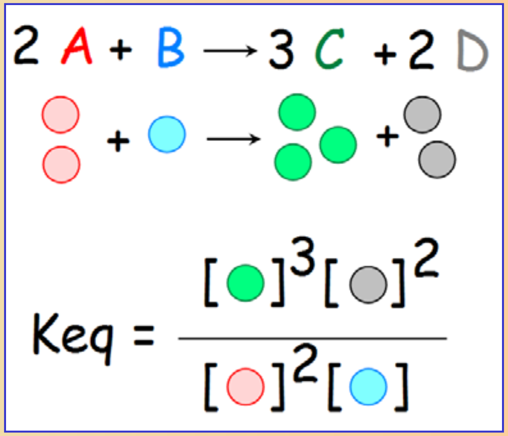
Equilibrium constant in terms of concentration (molarity)

The relationship between the concentrations of the reactants and products **at equilibrium** in any reaction can be established as follows:

$$a\,A + b\,B \rightleftarrows c\,C + d\,D$$

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

The subscript “c” indicates that concentrations (molarity) are used.



Rafa Muñoa
Lizardi Institutua
Zarautz

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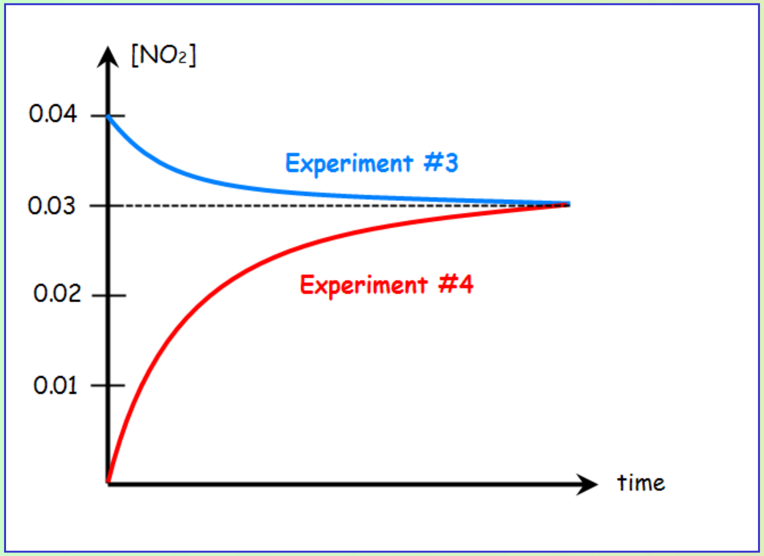
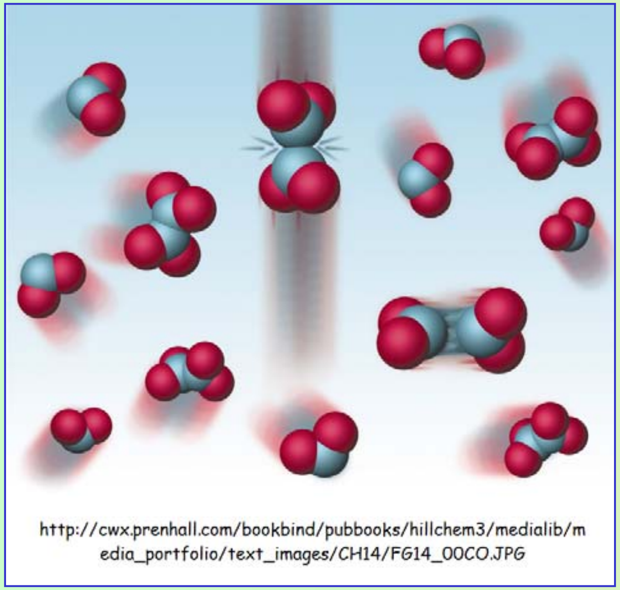


Equilibrium constant and initial concentrations

The value of the equilibrium constant at any given temperature does not depend on the initial concentrations of reactants and products.

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

$$Kc = \frac{[NO_2]^2}{[N_2O_4]} = 0.21 \quad (\text{at } T=100\ ^oC)$$



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Exper.	Initial $[N_2O_4]$	Initial $[NO_2]$	$[N_2O_4]$ at equil.	$[NO_2]$ at equil	Kc
1	0.00	0.02	0.00140	0.0172	0.21
2	0.00	0.03	0.00280	0.0243	0.21
3	0.00	0.04	0.00452	0.0310	0.21
4	0.02	0.00	0.00452	0.0310	0.21

Rafa Muñoa
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Zarautz

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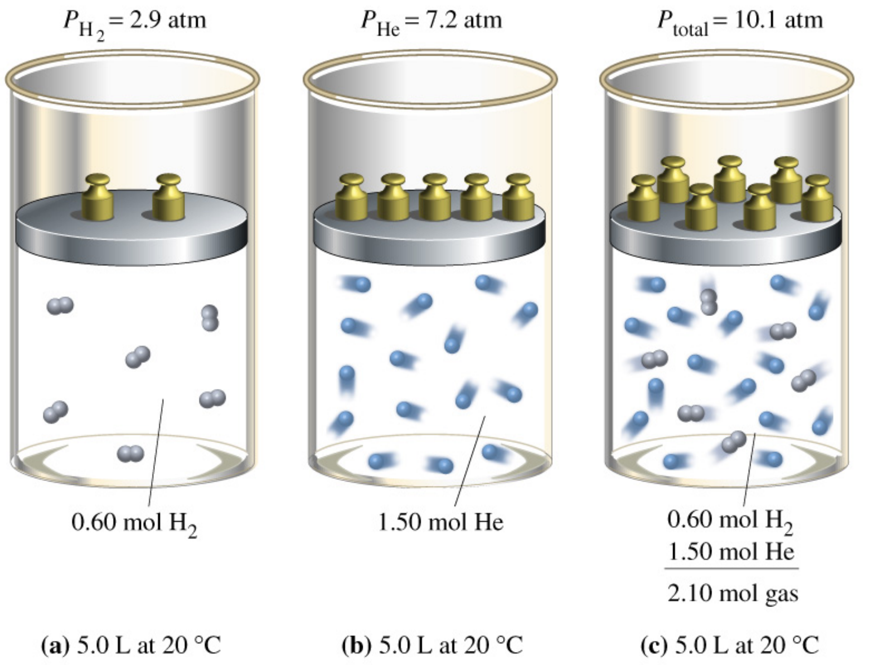

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Equilibrium constant in terms of pressure

When the reactants and products in a chemical equation are gases, we can formulate the equlibrium-constant expression in terms of partial pressures instead of molar concentrations.

When partial pressures in atmospheres are used in the expression, we denote the equilibrium constant as Kp:

$$a\,A + b\,B \rightleftarrows c\,C + d\,D$$

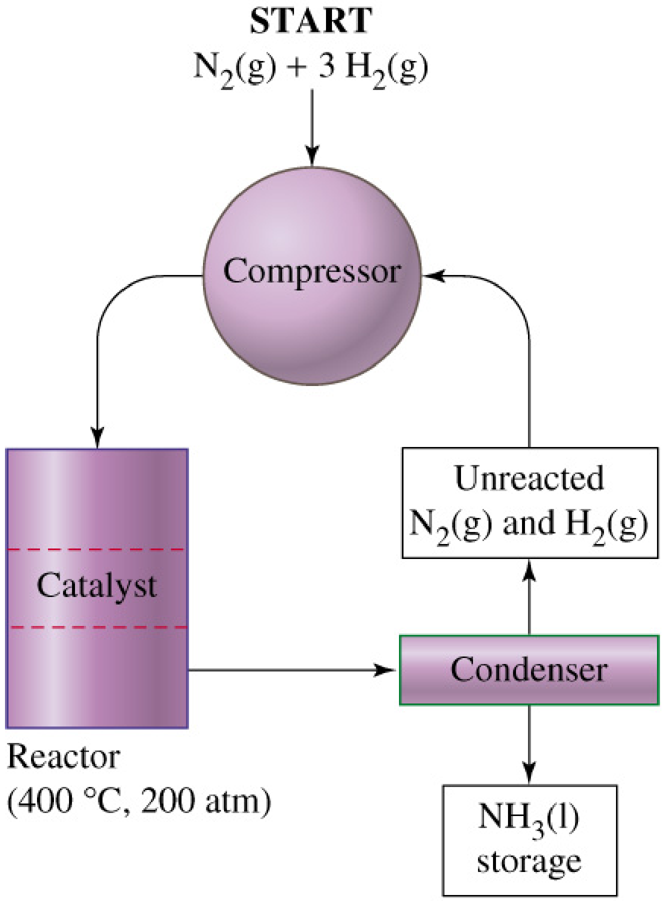
$$Kp = \frac{P_C^{\,c}\;P_D^{\,d}}{P_A^{\,a}\;P_B^{\,b}}$$

$$P_{H_2} = \frac{n_{H_2} * R * T}{V} = \frac{0.6 \text{ mol} * 0.082 \text{ atm.L/K.mol} * 293 \text{ K}}{5 \text{ L}} = 2.9 \text{ atm}$$

$$P_{He} = \frac{n_{He} * R * T}{V} = \frac{1.5 \text{ mol} * 0.082 \text{ atm.L/K.mol} * 293 \text{ K}}{5 \text{ L}} = 7.2 \text{ atm}$$

$$P_{tot} = \frac{n_{tot} * R * T}{V} = \frac{2.1 \text{ mol} * 0.082 \text{ atm.L/K.mol} * 293 \text{ K}}{5 \text{ L}} = 10.1 \text{ atm}$$

The equilibrium constant



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Relation between both equilibrium constants

For gaseous substances we can use the ideal-gas equation to convert between concentration (in molarity, M) and pressure (in atm):

$$PV = nRT \rightarrow P = \frac{n}{V}RT = MRT$$

M is concentration in mol/L

For substance “A” we can write: $P_A = [A]\,RT$

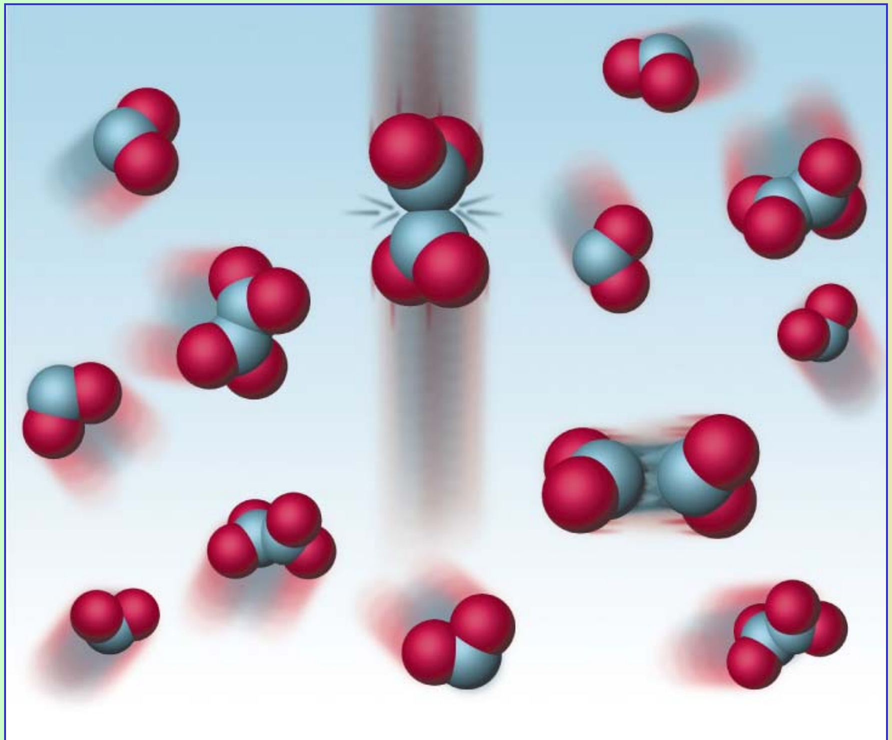
Therefore, the equivalence between both equlibrium constants is:

$$Kp = \frac{P_C^{\,c}\;P_D^{\,d}}{P_A^{\,a}\;P_B^{\,b}} = \frac{([C]RT)^c\;([D]RT)^d}{([A]RT)^a\;([B]RT)^b}$$

$$Kp = \frac{[C]^c\;[D]^d}{[A]^a\;[B]^b} * (RT)^{c+d-a-b} = Kc * (RT)^{\Delta n}$$

$$Kp = Kc * (RT)^{\Delta n} \quad \text{where } \Delta n = c+d-a-b$$

The equilibrium constant



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The direction of the chemical equation and K

Because an equilibrium can be approached from either direction, the direction in which we write the chemical equation is arbitrary.

The equilibrium constant for both directions are related.

For instance if

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

$$K = \frac{[NO_2]^2}{[N_2O_4]} = 0.212\ (\text{at } 100\ ^{o}C)$$

then we can affirm that

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

$$K = \frac{[N_2O_4]}{[NO_2]^2} = \frac{1}{0.212} = 4.72\ (\text{at } 100\ ^{o}C)$$