# Chemical Equilibria 1

| Reading: Ch 14 sections 1 - 5 | Homework: Chapter 14: 21*, 23, 25, 35*, 37, 39* |
|---|---|

* = ‘important’ homework question

## Background: Expressing Equilibria


Discussion: What is a *dynamic* chemical equilibrium?

Analogy: the Vancouver shoe sale

8:59 am: Before reaction starts

9:01 am: Reaction starts

9:10 am: *Dynamic* equilibrium established

**Product(s) and reactant(s) have fixed molar ratios at equilibrium**. Therefore:

***Forward* rate of reaction ≡ *Reverse* rate of reaction for a system at equilibrium**

Example: The Equilibrium between $N_2O_4$ (g) and the 'smog gas' $NO_2$ (g) - see slide.

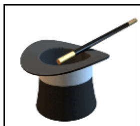
**Equilibrium Position**

Discussion: Based on the slide (as well as the above picture of the LA skyline), would you say that the equilibrium between $N_2O_4$ (g) and $NO_2$ (g) favors reactants or products at room temperature? Why?

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

The position (or condition) of a chemical equilibrium is expressed as a ratio of product(s) : reactant(s). This ratio is reported as a single quantity K, the equilibrium constant. Simply:

$$K = \frac{[\text{Product(s)}]}{[\text{Reactant(s)}]}$$



Typically: K > 1 for equilibria that favor product(s)
K < 1 for equilibria that favor reactant(s)

**Quantitative Determination of the Equilibrium Constant, K**

Task: Based on the basic definition of K, discussed above, *estimate** the value of K for the $N_2O_4$ (g) ⇔ 2 $NO_2$ (g) equilibrium via inspection of the supplied slide. What about the shoe store?

**A chemical equilibrium and its respective equilibrium expression are *quantitatively* related via the following generic expression:**

**For:** aA + bB ⇔ cC + dD

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

Important: The concentration of each reactant and product in a chemical equilibrium is raised to the power of its respective stoichiometic constant (balancing number), as found in the appropriate balanced chemical equation.

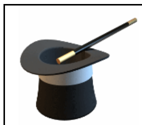
Task: Use the preceding math in conjunction with the slide to *determine** a more accurate value of K for the $N_2O_4$ (g) ⇔ 2 $NO_2$ (g) equilibrium.

**Note: For gas phase reactions, [conc] $\propto$ p**. Therefore, partial pressures (e.g. $p_{NO2}$ ) may be used in place of [conc] expressions for gas phase processes. See appendix for more examples.

Task: Write an expression for K, involving partial pressures, for:

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

Note: It is possible to mix 'n match [conc] and *p* units in a single equilibrium expression – this is an example of a *heterogeneous* equilibrium



Pure solids and/or liquids do NOT have a defined concentrations or partial pressures, so do NOT appear in equilibrium expressions

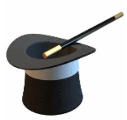
Example: Write an equilibrium expression for:

$$CaCO_3(s) + 2\ HCl\ (g) \Leftrightarrow CaCl_2\ (s) + H_2O\ (l) + CO_2\ (g)$$

Example: A mixture of $H_2$ (g) and $N_2$ (g) was allowed to come to equilibrium at 472 $^{o}$C:

$$N_2\,(g) + 3\,H_2\,(g) \Leftrightarrow 2\,NH_3\,(g)$$

Find K for this system, assuming the partial pressures or each reactant were found to be $p_{N2}$ = 2.46 atm, $p_{H2}$ = 7.38 atm, and be $p_{NH3}$ = 0.166 atm respectively.



If K is known for a chemical process, then the [conc] and/or partial pressures of aqueous and/or gas phase species, respectively, involved in a chemical process may be determined.

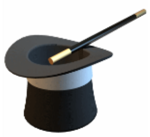
Example: At 21.8$^{o}$C, K for the following equilibrium is known to be 7.0 x $10^{-2}$.

$$NH_4HS\,(s) \Leftrightarrow NH_3\,(g) + H_2S\,(g)$$

Calculate the equilibrium partial pressures of $NH_3$ (g) and $H_2S$ (g) if a solid sample of $NH_4HS$ is placed in a closed vessel and allowed to decompose until equilibrium is attained. Is this a hetero- or homogeneous equilibrium? See appendix for another example.

The Feasibility of a Reaction – what does the value of K really mean?

Discussion: If K is very *large*, do reactants or products dominate at equilibrium? If K is very *small*, do reactants or products dominate at equilibrium? Hint: Recall the basic definition of K.



If K is *large*, the equilibrium is said to lie to the *right*.

If K is *small*, the equilibrium is said to lie to the *left*.

Extreme Cases – 'complete' and 'incomplete' reactions

**If $K \geq 10^{6}$, a reaction is said to be 'complete'**

**If $K \leq 10^{-6}$, a reaction is said to be 'incomplete'**

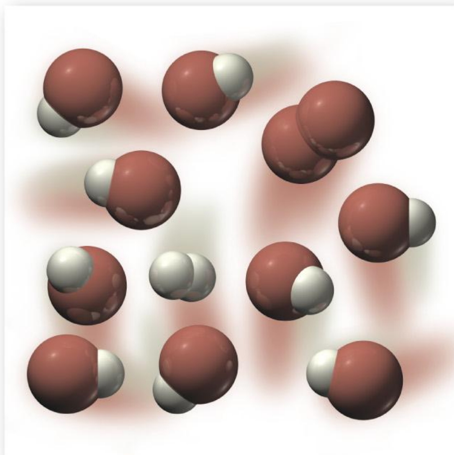
Discussion: Given the above information, is there such a thing as an entirely complete or incomplete chemical reaction??

Products

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

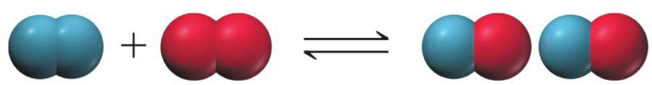
Reactants

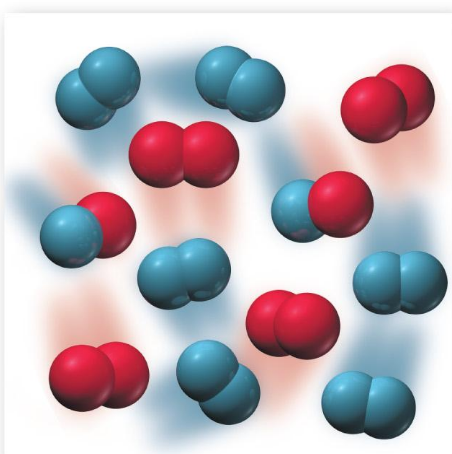
$$H_2(g) + Br_2(g) \rightleftharpoons 2\,HBr(g)$$



$$K = \frac{[HBr]^2}{[H_2][Br_2]} = \text{large number}$$

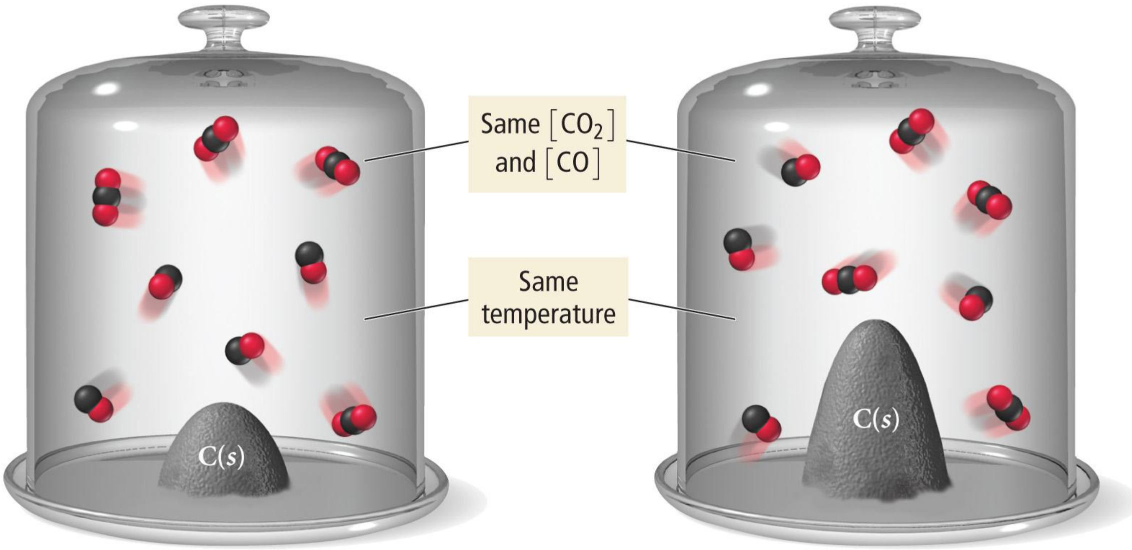
$$N_2(g) + O_2(g) \rightleftharpoons 2\,NO(g)$$





$$K = \frac{[NO]^2}{[N_2][O_2]} = \text{small number}$$

## A Heterogeneous Equilibrium




$$2\,CO(g) \rightleftharpoons CO_2(g) + C(s)$$