EQUILIBRIUM

INTRODUCTION: DEFINITIONS AND *K* VALUES

CHEMISTRY 165 // SPRING 2020

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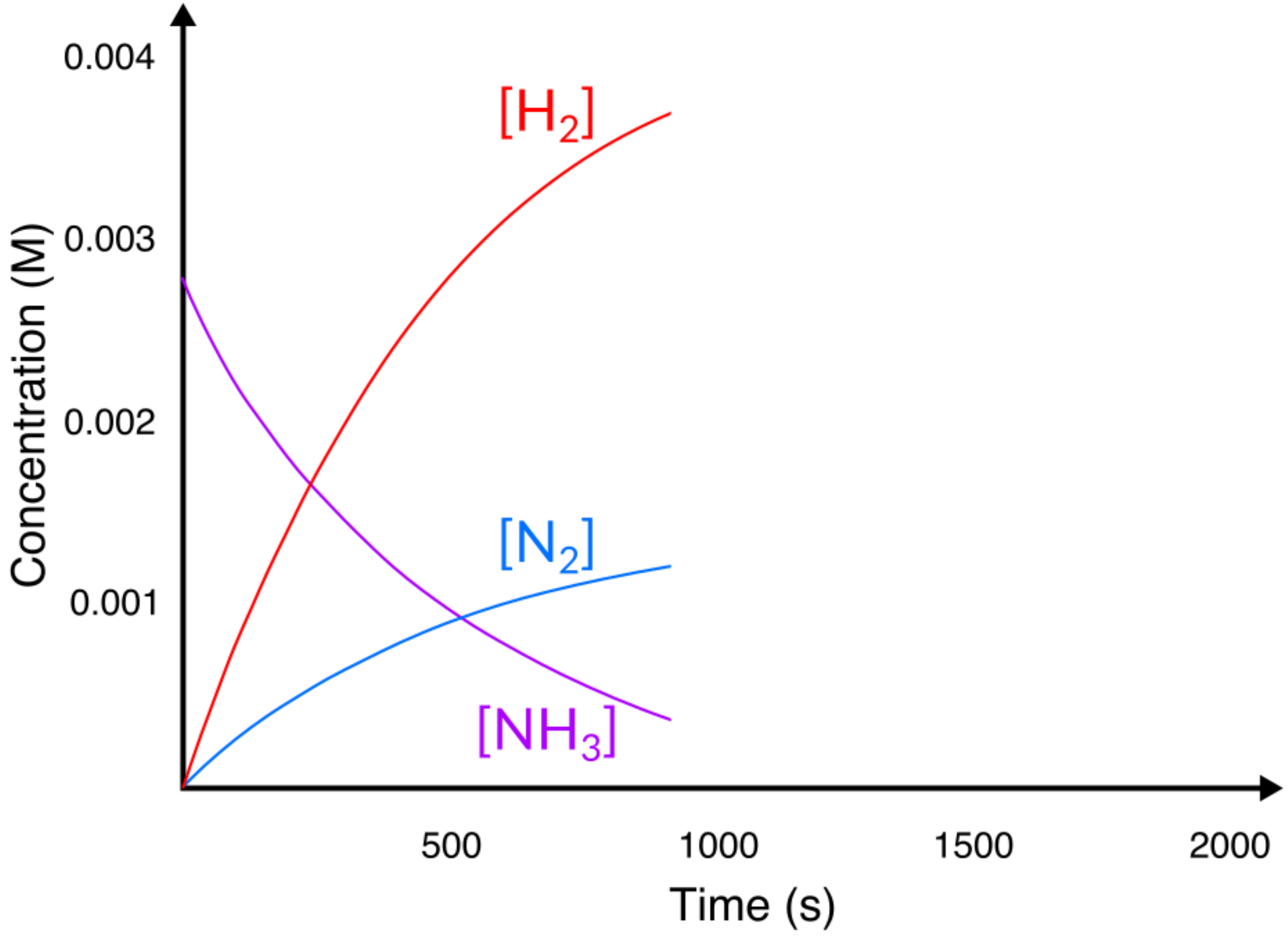
Chemical equilibrium

Consider the decomposition of ammonia gas into nitrogen gas and hydrogen gas.

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



Notice the arrow is unidirectional (→), which indicates the reaction proceeds in the direction to the right. This coincides with the plot of the concentrations over time since $[H_2]$ and $[N_2]$ increase and $[NH_3]$ decreases over time.

But what if we waited longer?

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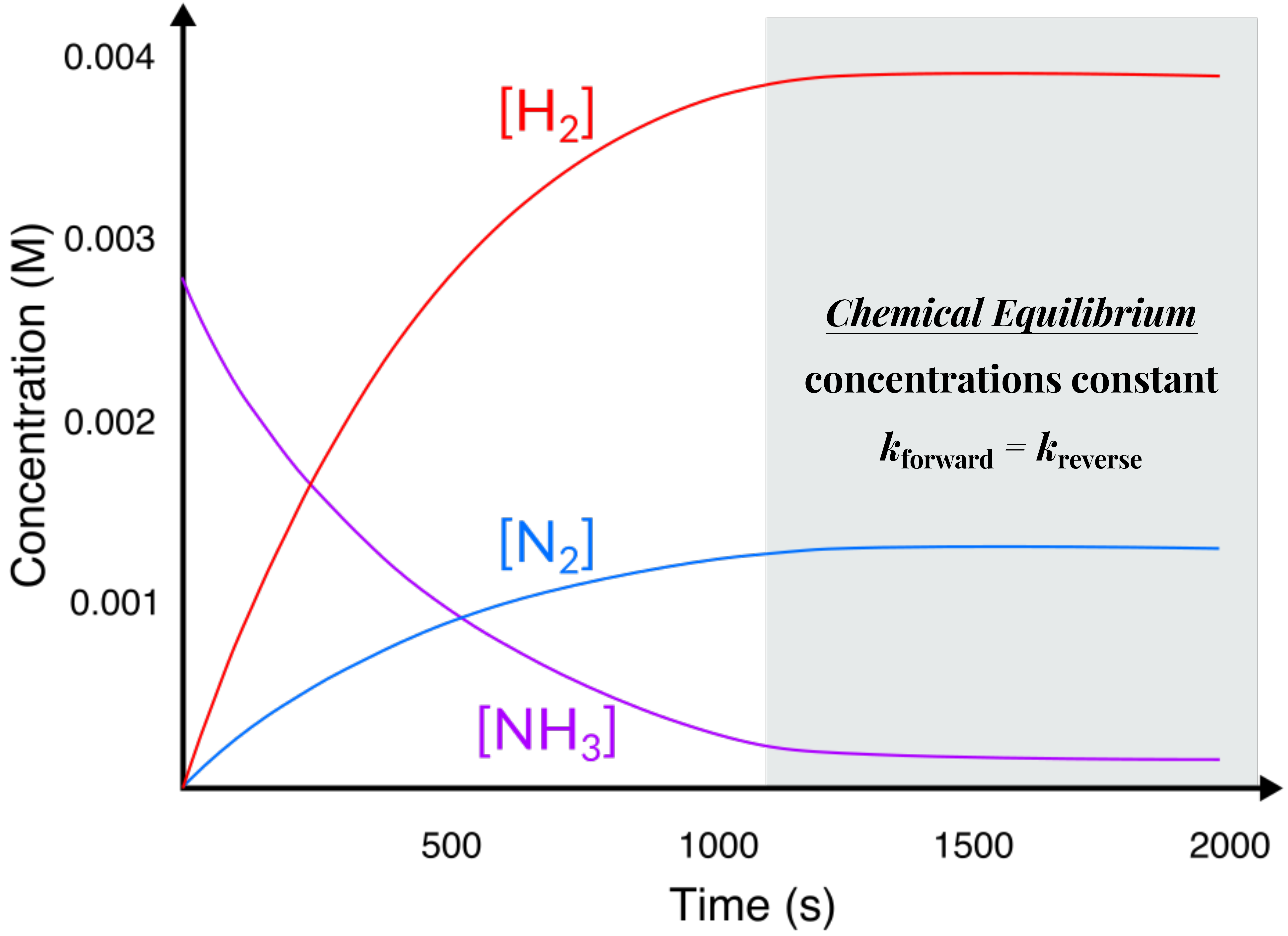

But what if we waited longer?

The concentrations would plateau rather than go to zero for the reactants. At this point, we reach chemical equilibrium. This is a dynamical process where NH_3 continues to decompose, but N_2 and H_2 will also re-combine to form NH_3 again. And the rates at which these forward and reverse processes occur are equal to each other.

$$k_{\text{forward}} = k_{\text{reverse}}$$

To better represent the dynamic nature of chemical reactions that reach equilibrium we use the $\rightleftharpoons$ arrow to indicate both processes occurring.

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

Quantifying equilibrium: K_c values

As it turns out, regardless of what initial conditions (concentrations) we start with we always end up at equilibrium. This behavior means suggests that we can express equilibrium quantitatively through an equilibrium constant (K).

Consider the general balanced chemical equation:

$$a\text{ A} + b\text{ B} \rightleftharpoons c\text{ C} + d\text{ D}$$

The equilibrium constant for this reaction is expressed using the Law of Mass Action and is a ratio between the amount of products to reactants:

This is the equilibrium constant. → $$K_c = \frac{[\text{C}]^c[\text{D}]^d}{[\text{A}]^a[\text{B}]^b}$$ ← **These powers are the coefficients in the balanced chemical equation.**

This "c" subscript tells us we need use concentrations.

These are concentrations at equilibrium.

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If the equilibrium were among only gases, we could also write another equilibrium constant:

$$a\,\mathrm{A}\,(g) + b\,\mathrm{B}\,(g) \rightleftharpoons c\,\mathrm{C}\,(g) + d\,\mathrm{D}\,(g)$$

$$K_\mathrm{p} = \frac{P_\mathrm{C}^c P_\mathrm{D}^d}{P_\mathrm{A}^a P_\mathrm{B}^b}$$

This is the equilibrium constant. → K_p

These powers are the coefficients in the balanced chemical equation.

This "p" subscript tells us we need use partial pressures.

These are partial pressures at equilibrium.

Features of K_c and K_p

Despite the forms of the equilibrium constants, they are unitless/dimensionless quantities.

Additionally, for gaseous equilibria we can convert between K_c and K_p via the ideal gas law to re-express partial pressures in terms of concentrations. Here I show it for a gas compound C.

$$P_C V = n_C RT$$

$$P_C = \frac{n_C}{V} RT$$

$$P_C = [C]RT$$

Now, we can substitute our partial pressures in the K_p expression for concentrations and derive the relationship between K_c and K_p:

$$K_p = \frac{P_C^c P_D^d}{P_A^a P_B^b} = \frac{([C]RT)^c([D]RT)^d}{([A]RT)^a([B]RT)^b} = \underbrace{\frac{[C]^c[D]^d}{[A]^a[B]^b}}_{\text{This is } K_c!} \cdot \frac{(RT)^{c+d}}{(RT)^{a+b}} = K_c \cdot (RT)^{\Delta n}$$

Remember these powers are just the coefficients in the balanced chemical equation, so:

$$\boldsymbol{\Delta n = (c + d) - (a + b)}$$

This Δn is just the change in the number of moles of products and reactants!

Manipulating *K* values

Because the K values are written based on the balanced chemical equation, K values can be different depending on how you balance the equation.

For instance, consider the three balanced chemical equations and their K_c values at 425 K.

I_2 (g) + Br_2 (g) ⇌ 2 IBr (g)

$$K_c = \frac{[IBr]^2}{[I_2][Br_2]} = 120.$$

½ I_2 (g) + ½ Br_2 (g) ⇌ IBr (g)

$$K_c' = \frac{[IBr]}{[I_2]^{1/2}[Br_2]^{1/2}} = 11.0$$

2 I_2 (g) + 2 Br_2 (g) ⇌ 4 IBr (g)

$$K_c'' = \frac{[IBr]^4}{[I_2]^2[Br_2]^2} = 1.44\times10^4$$

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Luckily, the relationship between the different K_c values is just related to the quantity (n) by which we multiple the first balanced equation. The other K_c values are simply mathematical manipulations of K_c^n.

$I_2(g) + Br_2(g) \rightleftharpoons 2\,IBr(g)$ $$K_c = \frac{[IBr]^2}{[I_2][Br_2]} = 120.$$

×1/2

×2

$\frac{1}{2} I_2(g) + \frac{1}{2} Br_2(g) \rightleftharpoons IBr(g)$ $$K_c' = \frac{[IBr]}{[I_2]^{1/2}[Br_2]^{1/2}} = 11.0$$

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$$K_c' = (K_c)^{1/2}$$
$$K_c'' = (K_c)^2$$

PRACTICE PROBLEM 1

At 1200 K, the partial pressures of an equilibrium mixture of H_2O, H_2, and O_2 gases are 0.040, 0.0045, and 0.0030 atm, respectively. Calculate the value of the equilibrium constant K_p for the reaction at 1200 K.

$$2\ H_2O\ (g) \rightleftharpoons 2\ H_2\ (g) + O_2\ (g)$$

— answer —

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$$\begin{aligned} K_p &= \frac{P_{H_2}^2 P_{O_2}}{P_{H_2O}^2} \\ &= \frac{(0.0045)^2(0.0030)}{(0.040)^2} \\ K_p &= 3.8\times10^{-5} \end{aligned}$$

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At 1200 K, the partial pressures of an equilibrium mixture of H_2O, H_2, and O_2 gases are 0.040, 0.0045, and 0.0030 atm, respectively. Calculate the value of the equilibrium constant K_p for the reaction at 1200 K. Now calculate the K_c value.

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$$K_p = 3.7_9 \times 10^{-5}$$

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$$K_{\text{p}} = K_{\text{c}}(RT)^{\Delta n}$$
$$3.7_9 \times 10^{-5} = K_{\text{c}}(0.08206 \times 1200)^1$$

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We can convert from K_p to K_c via:

$$\begin{aligned} K_\mathrm{p} &= K_\mathrm{c}(RT)^{\Delta n} \\ 3.7_9 \times 10^{-5} &= K_\mathrm{c}(0.08206 \times 1200)^1 \\ K_\mathrm{c} &= 3.9 \times 10^{-7} \end{aligned}$$

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PRACTICE PROBLEM 3

At equilibrium, the concentrations of gaseous N_2, O_2, and NO in a container are $[N_2]$ = 3.3 M, $[O_2]$ = 5.8 M, and [NO] = 3.1 M. Calculate the value of K_c for this reaction.

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

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$$K_c = \frac{[NO]^2}{[N_2][O_2]}$$

$$= \frac{(3.1)^2}{(3.3)(5.8)}$$

$$K_c = 0.50$$

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Recognize that the reverse process would be:

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Understand that the relationship between the forward and reverse *K* expression is simply:

$$K_c^{reverse} = \frac{1}{K_c^{forward}}$$

PRACTICE PROBLEM 5

Calculate the value of K_p at 298 K for the reaction

$$N_2\,(g) + 2\,O_2\,(g) \rightleftharpoons 2\,NO_2\,(g)$$

From the following two K_p values at 298K.

(1) $N_2\,(g) + O_2\,(g) \rightleftharpoons 2\,NO\,(g)$ $\quad K_p^{(1)} = 4.4 \times 10^{-31}$

(2) $2\,NO\,(g) + O_2\,(g) \rightleftharpoons 2\,NO_2\,(g)$ $\quad K_p^{(2)} = 2.4 \times 10^{12}$

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Similar to Hess's Law, we can combine equations (1) and (2) together.

$$\begin{array}{llllll} & N_2\,(g) & + & O_2\,(g) & \rightleftharpoons & \cancel{2\,NO}\,(g) & K_p^{(1)} \\ + & \cancel{2\,NO}\,(g) & + & O_2\,(g) & \rightleftharpoons & 2\,NO_2\,(g) & K_p^{(2)} \\ \hline \end{array}$$

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Similar to Hess's Law, we can combine equations (1) and (2) together. But, to find the combined Kp involves multiply (instead of addition) and division (instead of subtraction).

$$\begin{array}{lcccccl} & N_2\,(g) & + & O_2\,(g) & \rightleftharpoons & \cancel{2\,NO}\,(g) & K_p^{(1)} \\ + & \cancel{2\,NO}\,(g) & + & O_2\,(g) & \rightleftharpoons & 2\,NO_2\,(g) & K_p^{(2)} \\ \hline & N_2\,(g) & + & 2\,O_2\,(g) & \rightleftharpoons & 2\,NO_2\,(g) & K_p = K_p^{(1)} \times K_p^{(2)} \end{array}$$

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$$= (4.4 \times 10^{-31})(2.4 \times 10^{12})$$

$$K_p = 1.1 \times 10^{-18}$$