EQUILIBRIUM

LE CHATELIER'S PRINCIPLE & REACTION QUOTIENTS (Q)

CHEMISTRY 165 // SPRING 2020

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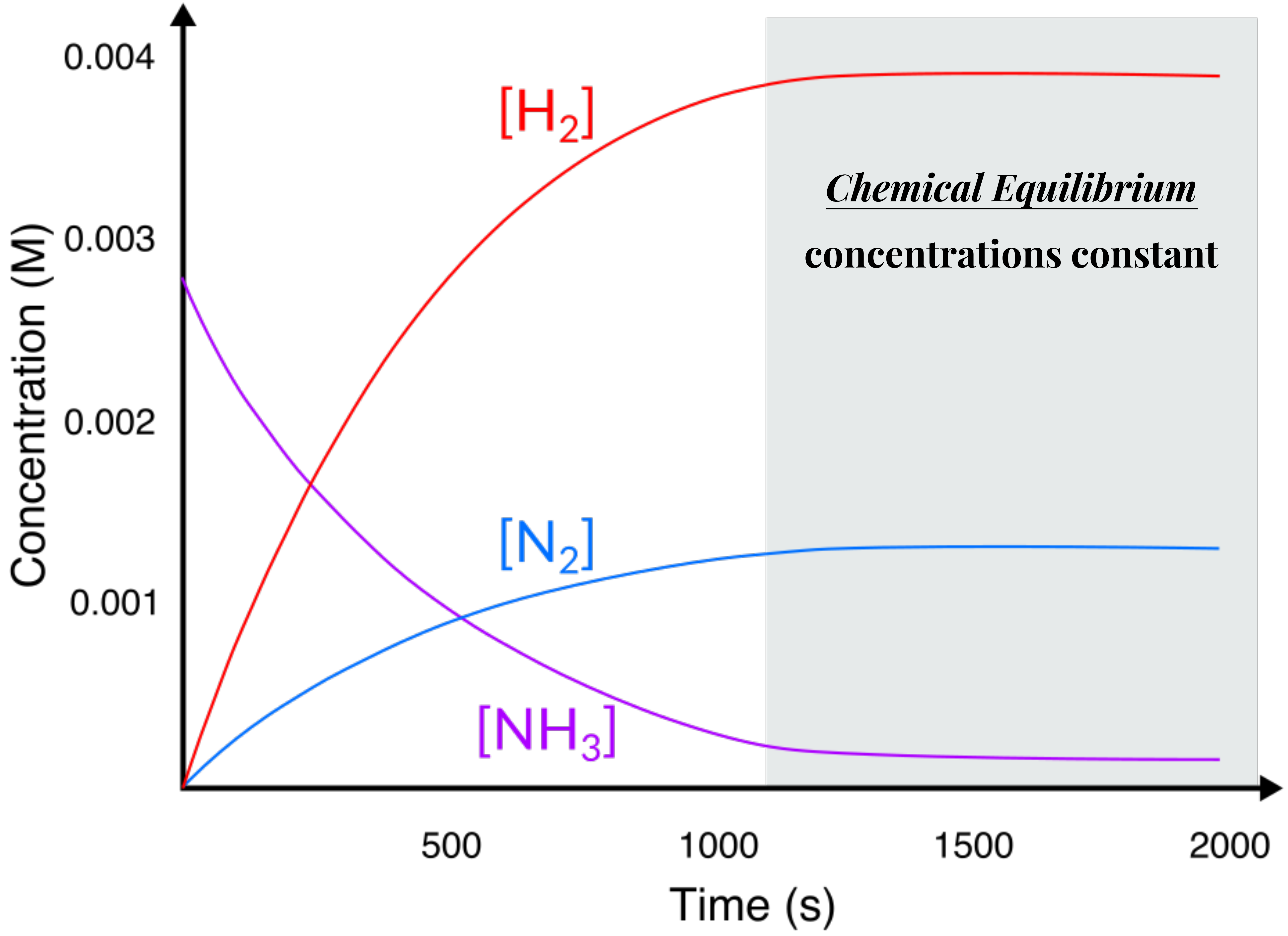
Am I at equilibrium or not?

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

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



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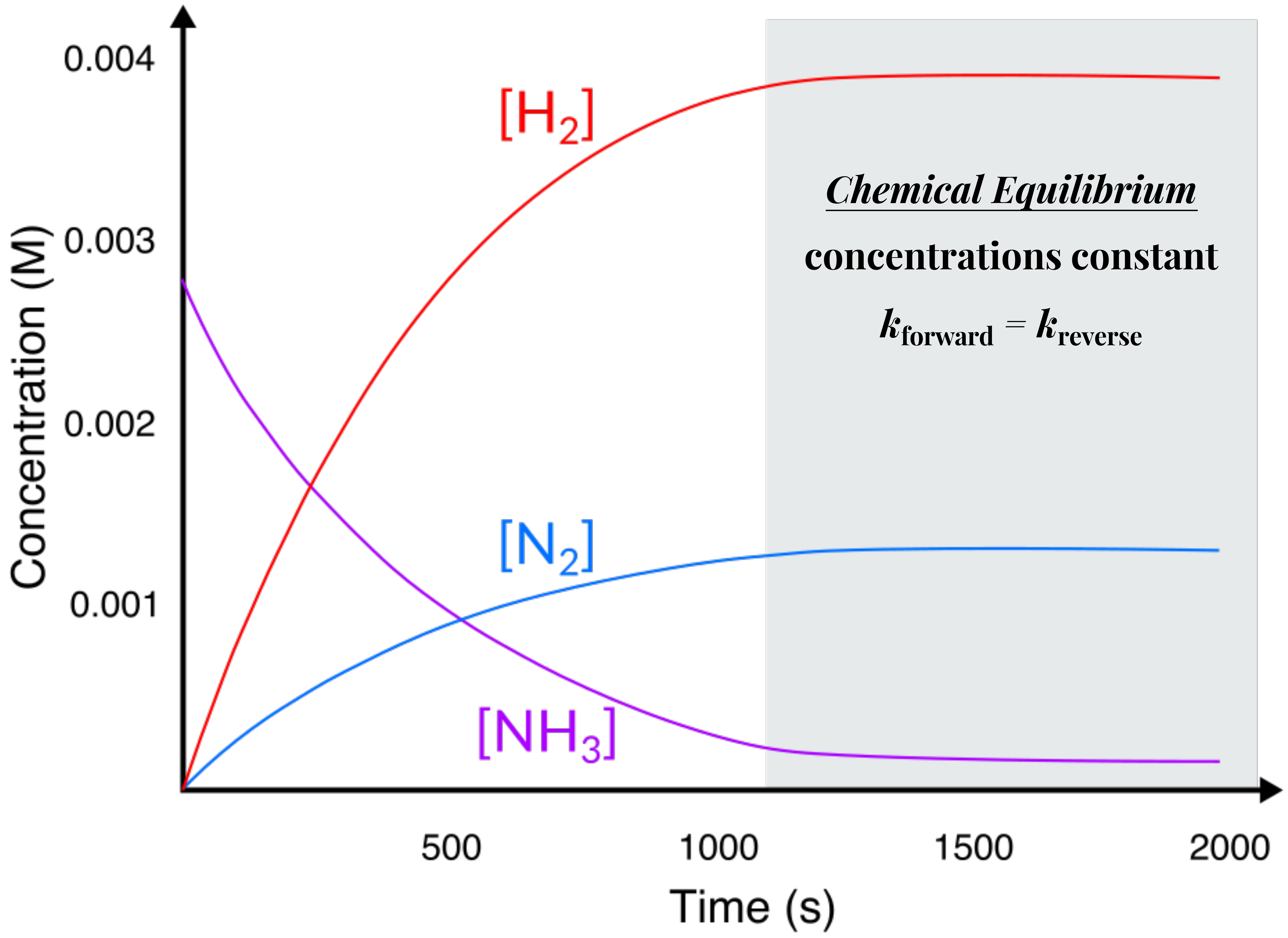

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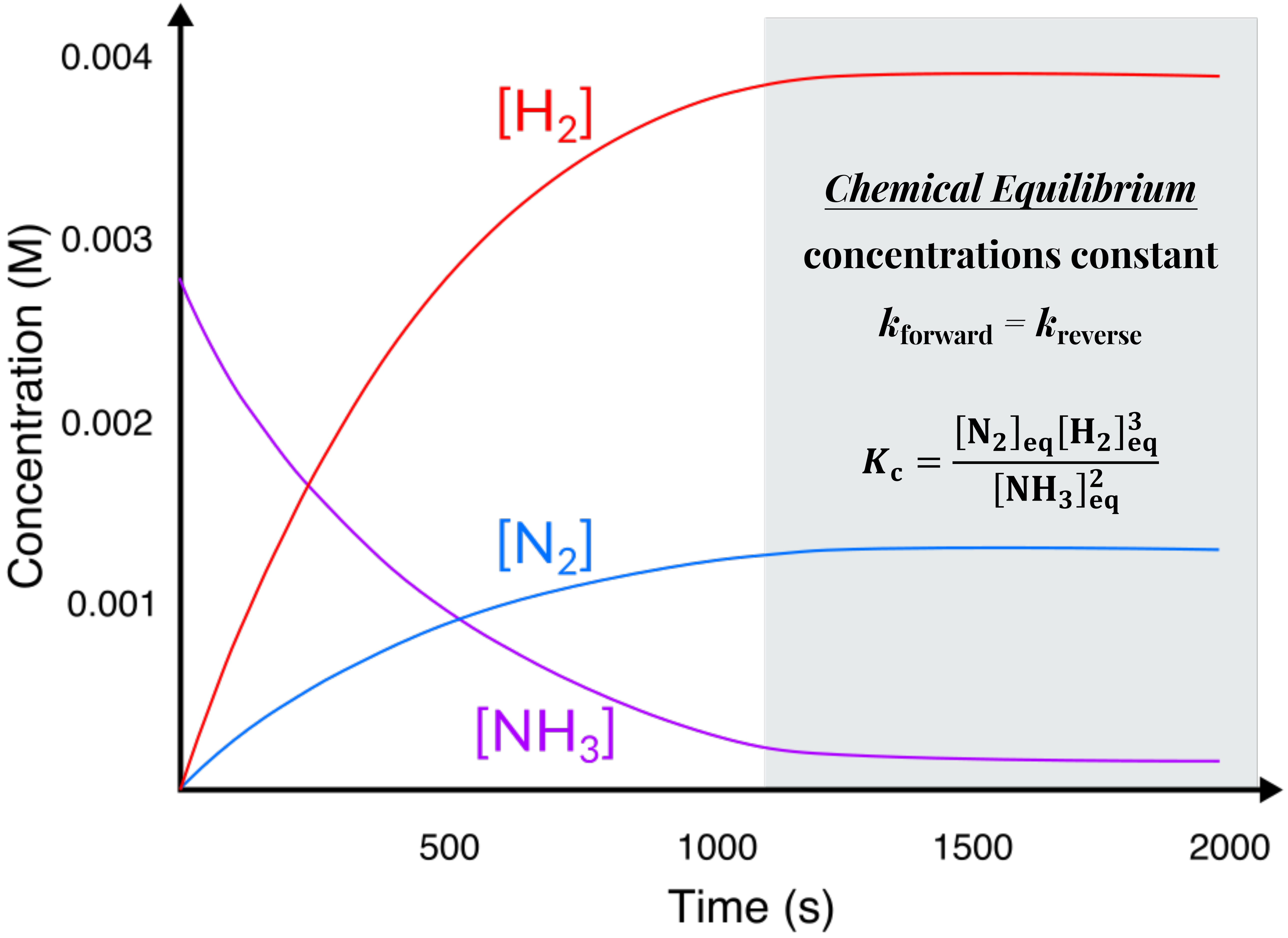

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A better way is calculate a reaction quotient (Q), which has the same form as the K_c value.

$$Q = \frac{[N_2]_t[H_2]_t^3}{[NH_3]_t^2}$$

The system will be at equilibrium if:

$$Q = K_c$$

What if my Q ≠ K?

Systems have a natural tendency to go toward equilibrium, where Q = K.

So, if Q ≠ K, the system will undergo some change to reach equilibrium.

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Consider the following graphical representation:

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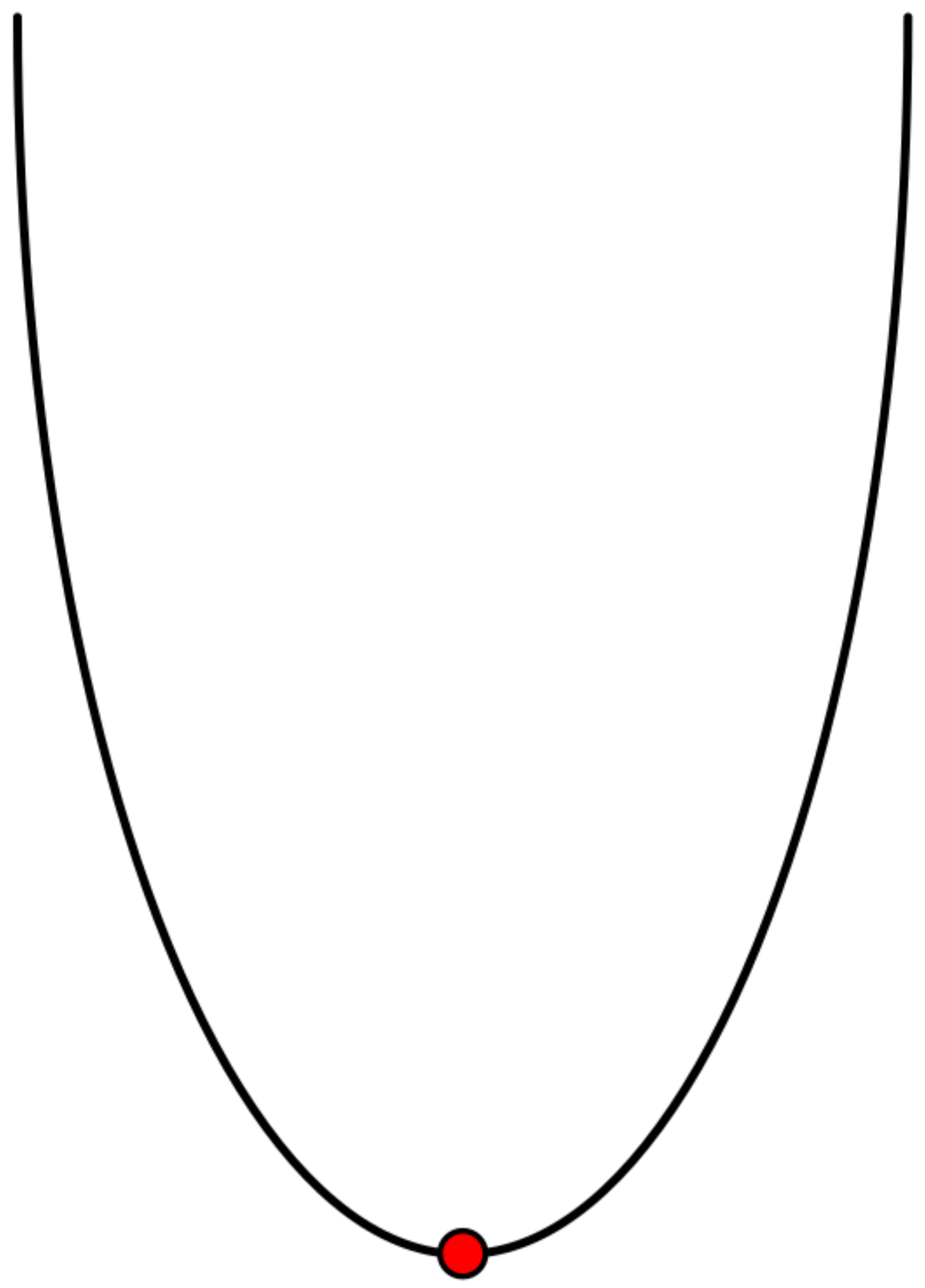

Q = K

(at equilibrium)

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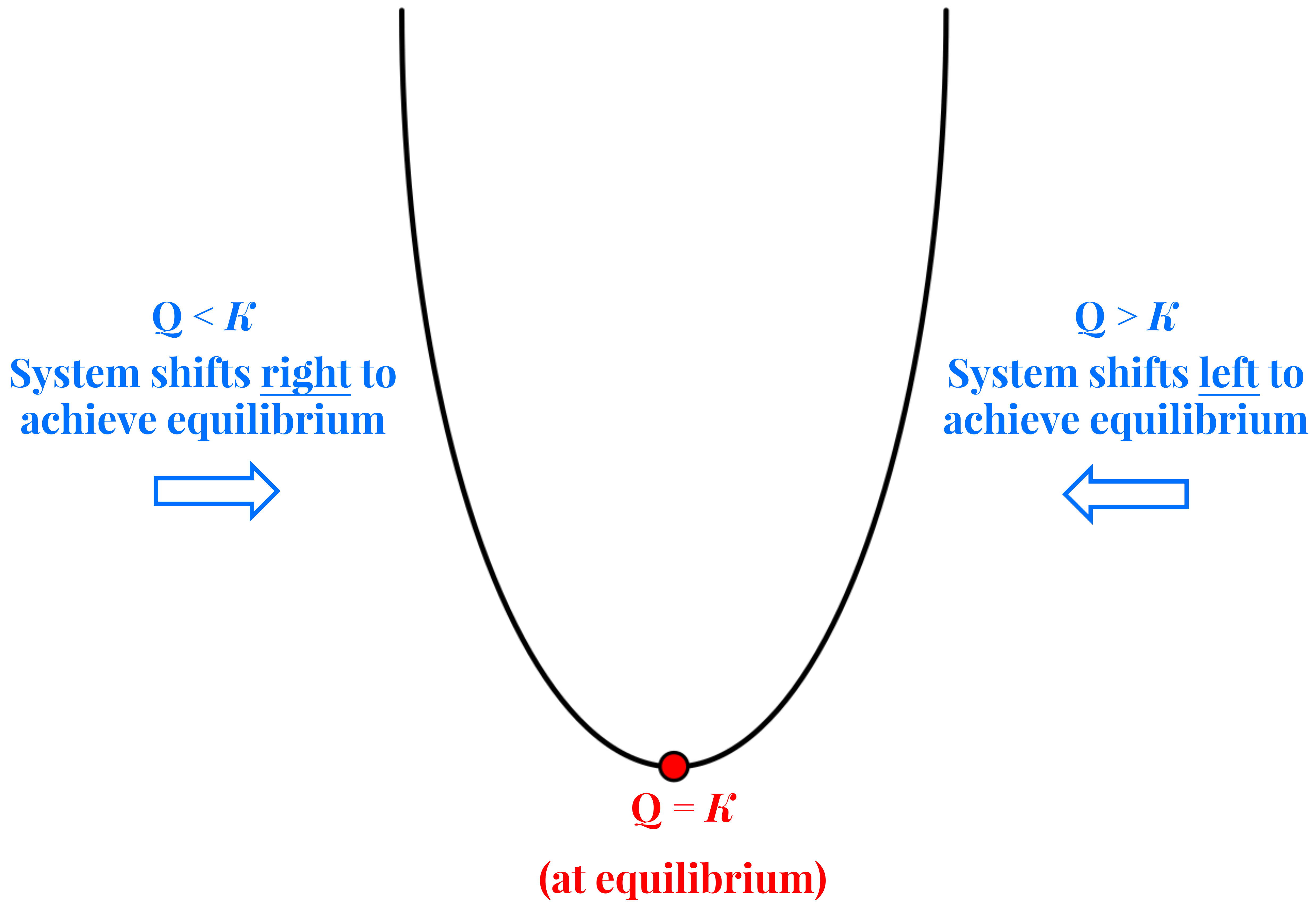
- If Q > K, then the amount of products is greater than reactants, so our system will shift toward the left to use up N_2 and H_2 and make more NH_3.
- If Q < K, then the amount of reactants is greater than products, so our system will shift toward the right to use up NH_3 and make more N_2 and H_2.



PRACTICE PROBLEM

Given below are the initial concentrations of reactants and products for three experiments involving the reaction:

$$CO\ (g) + H_2O\ (g) \rightleftharpoons CO_2\ (g) + H_2\ (g) \qquad K_c = 0.64$$

Determine in which direction the reaction will proceed to reach equilibrium in each of the experiments.

— answer —

First, write the expression for the reaction quotient:

$$Q = \frac{[CO_2][H_2]}{[CO][H_2O]}$$

For each experiment, calculate the reaction quotient (Q), and compare to K_c to determine the shift in the reaction.

	Experiment 1	Experiment 2	Experiment 3
$[CO]_0$	0.0203 M	0.011 M	0.0094 M
$[H_2O]_0$	0.0203 M	0.0011 M	0.0025 M
$[CO_2]_0$	0.0040 M	0.037 M	0.0015 M
$[H_2]_0$	0.0040 M	0.046 M	0.0076 M

$$Q_1 = \frac{(0.0040)(0.0040)}{(0.0203)(0.0203)}$$
$$Q_1 = 0.039$$

$$Q_2 = \frac{(0.037)(0.046)}{(0.011)(0.0011)}$$
$$Q_2 = 1.4\times10^2$$

$$Q_3 = \frac{(0.0015)(0.0076)}{(0.0094)(0.0025)}$$
$$Q_3 = 0.48$$

$Q_1 < K_c$
(shift right)

$Q_1 > K_c$
(shift left)

$Q_3 < K_c$
(shift right)

Le Chatelier's Principle

Chemical systems will tend toward equilibrium (Q = K) in response to any stress placed upon the system.

We've already seen how concentrations can affect the shift in reaction directions, but what about other effects?

Consider the gaseous equilibrium: $N_2O_4\ (g) \rightleftharpoons 2\ NO_2\ (g)$

$$Q_c = \frac{[NO_2]^2}{[N_2O_4]} \quad \text{or} \quad Q_p = \frac{P_{NO_2}^2}{P_{N_2O_4}}$$

	Change	Q initial	Shift
Concentration	Increase $[N_2O_4]$	Q < K	right
	Increase $[NO_2]$	Q > K	left
	Decrease $[N_2O_4]$	Q > K	left
	Decrease $[NO_2]$	Q < K	right
Pressure	Increase pressure	Q > K	left (to side with less moles of gas)
	Decrease pressure	Q < K	right (to side with more moles of gas)
Volume	Increase volume	Q < K	right (to side with more moles of gas)
	Decrease pressure	Q > K	left (to side with less moles of gas)

$$V \propto \frac{1}{P}$$

$$P \propto n$$

Temperature effects

Le Chatelier's principle tells us that when we introduce a change/stress into our system that changes our reaction quotient (Q), the system/reaction will shift left or right to establish equilibrium (Q = *K*).

The effect of temperature actually changes the value of *K* itself. But we can still apply Le Chatelier's principle to predict the direction of the change.

Exothermic reactions

$H_2\ (g) + I_2\ (g) \rightleftharpoons 2\ HI\ (g)$ $\Delta H = -9.4$ kJ

For exothermic reactions, we can treat the heat *released* like a product:

$H_2\ (g) + I_2\ (g) \rightleftharpoons 2\ HI\ (g) + \text{heat}$

- If we increase heat, the reaction shifts left since Q > K because K decreases.
- If we decrease heat, the reaction shifts right since Q < K because K increases.

Endothermic reactions

$N_2O_4\ (g) \rightleftharpoons 2\ NO_2\ (g)$ $\Delta H = +57.2$ kJ

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Endothermic reactions

N_2O_4 (g) ⇌ 2 NO_2 (g) $\Delta H = +57.2$ kJ

For endothermic reactions, we can treat the heat *absorbed* like a reactant:

heat + N_2O_4 (g) ⇌ 2 NO_2 (g)

- If we increase heat, the reaction shifts right since Q < K because K increases.
- If we decrease heat, the reaction shifts left since Q > K because K decreases.