Kinetics versus Equilibrium

Speed of the reaction
how fast or slow the reaction happens

does not say anything about how fast the rxn. proceeds

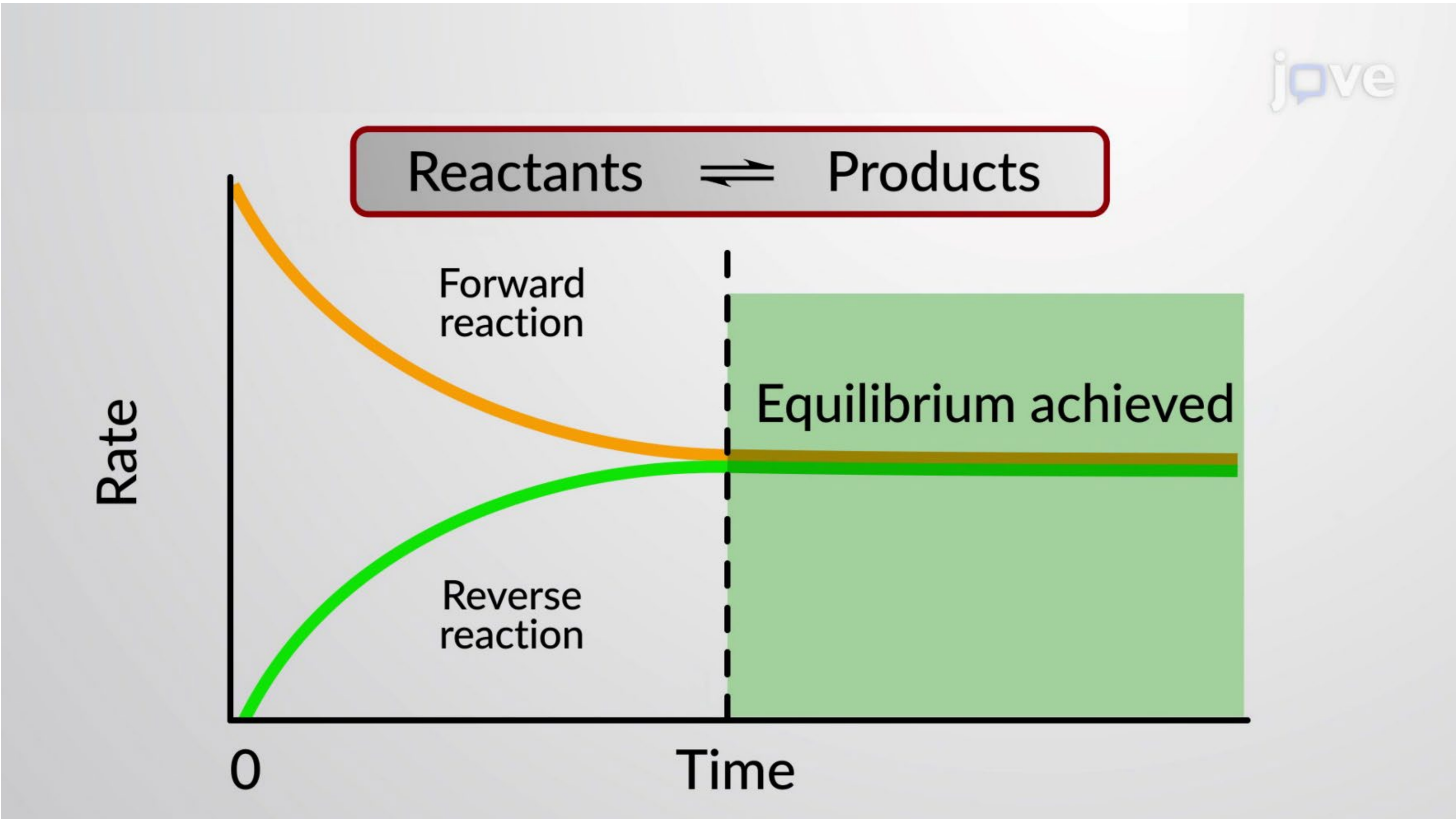
$\rightleftharpoons$

· whether the reaction @ $\rightleftharpoons$ is reactant or product favored

@ $\rightleftharpoons$ rate for = rate = rev.

At equilibrium

rate forward reaction = rate of reverse reaction



Derivation of equilibrium constant (Keq)

(a) $\rightleftharpoons$ ratefor = raterev

$$aA + bB \underset{k_r}{\overset{k_f}{\rightleftharpoons}} cC + dD$$

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

"new" term

$$K_{eq} = \frac{K_f}{K_r}$$

$$\frac{K_f}{K_r}\left(\frac{[A]^a[B]^b}{[C]^c[D]^d}\right) = 1$$

$$K_{eq}\left(\frac{[A]^a[B]^b}{[C]^c[D]^d}\right) = 1$$

$$\therefore \boxed{K_{eq}} = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

"unitless"

if $K_{eq} > 1$ product favored @ eq

$$aA + bB \rightleftharpoons cC + dD$$

if $K_{eq} < 1$ reactant favored @ eq

$K = 1$ neither reactant or product favored

Writing equilibrium expressions

- **Solids and liquids are not included in equilibrium expression!**

only including gases or aq. solutions

- **Write equilibrium expression for the following eq reactions**

$PV = nRT$

gases can measure partial pressure or concentration, M

$P = \frac{n}{V} RT$

- If K is > 1 the reaction is product or reactant favored?

- If K<1 the reaction is reactant or product favored

$$CaCO_{3(s)} \rightleftharpoons Ca^{2+}_{(aq)} + CO_{3(aq)}^{2-}$$

$$K_{eq} = \underbrace{[Ca^{2+}][CO_3^{2-}]}$$

$K_{\underline{c}}$ ☆ use molarity

$K_{\underline{p}}$ ☆ use pressure

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$$

write an equilibrium expression, K_c.

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

write for K_p

$$K_p = \frac{P_{NH_3}^{\,2}}{P_{N_2} P_{H_2}^{\,3}}$$

- Gases can be expressed in terms of pressure or concentration

Kc eq constant using concentration, M

Kp eq constant using pressure, atm

What is the relationship between Kp and Kc?

$$\boxed{Kp = Kc\,(RT)^{\Delta n}}$$

Δn = moles of products – moles of reactants
*gases only!

K_c is equal to 0.28 for the following reaction at 900 °C

$$\underbrace{CS_2(g)+4H_2(g)}_{5\text{mol}} \rightleftharpoons \underbrace{CH_4(g)+2H_2S(g)}_{3\text{mol}}$$

What is Kp ?

$$K_p = K_c\,(RT)^{\Delta n}$$

$$\Delta n = -2$$

$$K_p = 0.28\,(0.08206 \times 1{,}173)^{-2}$$

$$\boxed{3 \times 10^{-5}}$$

Calculating K from equilibrium concentrations

The reaction between gaseous sulfur dioxide and oxygen (gas) produces sulfer trioxide gas.

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

The equilibrium mixture contained 0.0500 M SO_3, and 0.00350 M O_2 0.00300 M SO_2, @ 800K. Calculate K_c

$$K_c = \frac{[SO_3]^2}{[SO_2]^2 [O_2]^1}$$

Calculating Equilibrium concentrations continued

$$K_c = \frac{(0.0500)^2}{(0.00300)^2(0.0035)^1}$$

product favored @ eq.

version 1

$$K_c = 7.94 \times 10^4$$

* calculating K given all eq. [ ]

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version 2

Calculating K given only one concentration @ equilibrium

A 1.0 mol sample of NOCl was placed in a 2.00 L reactor and decomposed @ 227°C.

$$2NOCl_{(g)} \rightleftharpoons 2NO_{(g)} + Cl_{2(g)}$$

At equilibrium, there was 0.056 mol of Cl_2.
What is K_c?

Calculating Equilibrium Concentrations Part II

What if the initial concentration is given some reactants and products?

Need to determine the reaction quotient "Q" and the direction the reaction will shift to reach equilibrium

Calculate Q using the initial concentration of reactants and products

$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$

Example:
For the synthesis of ammonia at 500°C the K_c is 6.0×10^{-2}.

If the initial $[NH_3]$ is 3.00×10^{-2} M, $[N_2]$ and $[H_2]$ is 2.00×10^{-3} M which direction will the reaction shift to reach eq.?

when... $Q = K$

$Q < K$

$Q > K$

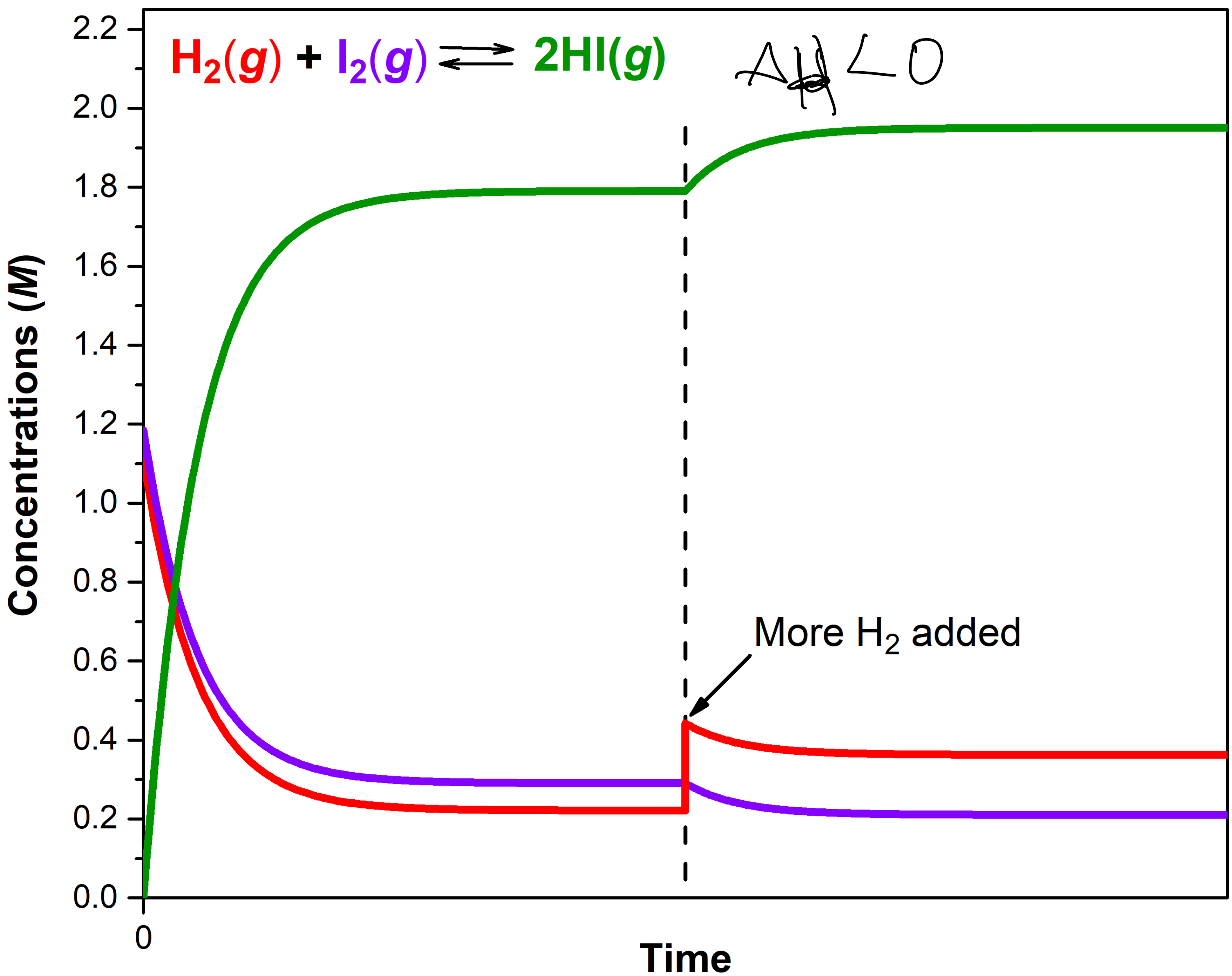
Calculating Equilibrium Concentrations Part III

- A 1.00 L flask initially contains 0.298 mol of PCl_3 (g) and 8.70 x 10^{-3} mol of PCl_5 (g) . After the system reaches equilibrium, 2.00 x 10^{-3} mol of chlorine gas was in the flask. Calculate the equilibrium concentrations of all species and K_c

$$PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$$

Equilibrium Part III

Le Chatelier's Principle



Le Chateliers Principle Examples

concentration

pressure or volume

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

temperature