Kinetics versus Equilibrium

Speed of the reaction
how fast or slow the reaction happens

does not say anything about how fast the rxn. proceeds

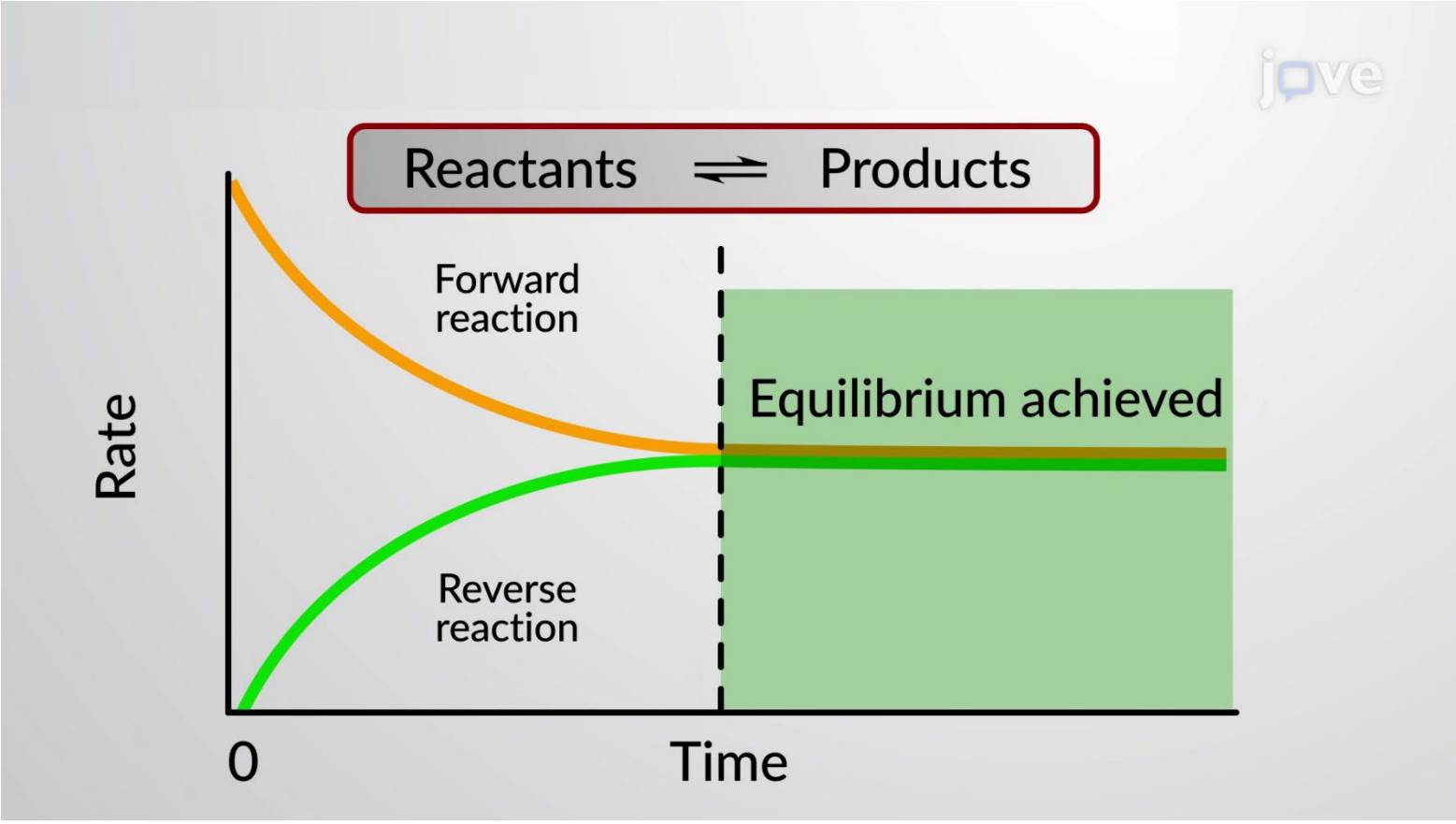
$\rightleftharpoons$

- 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)

ⓐ $\rightleftharpoons$ rate for = rate rev

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

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

"new" term $K_{eq} = \frac{k_f}{k_r}$

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

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

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

"unitless"

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

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

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

$K = 1$ neither reactant 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

$$CaCO_{3(s)} \rightleftharpoons Ca^{2+}_{(aq)} + CO_3^{2-}{}_{(aq)}$$

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

K_c ★ use molarity

K_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

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

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

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

what is the new K_p if the reaction is reversed?

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

$$K_{p\text{"new"}} = \frac{P_{N_2} P_{H_2}^3}{P_{NH_3}^2}$$

$$K_{pnew} = \frac{1}{K_p}$$

- 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?

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

Δn = moles of products – moles of reactants

*gases only!

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

5mol 3mol

$CS_2(g)+4H_2(g) \rightleftharpoons CH_4(g)+2H_2S(g)$

What is Kp ?

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

$\Delta n = -2$

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

3×10^{-5}

Calculating K from equilibrium concentrations

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

- $2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$

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

$K_c = 7.94 \times 10^4$

* calculating K given all eq. [ ]

version 1

version 2

Calculating K given only one concentration @ equilibrium

A 1.0 mol sample of NOCl was placed in a 2.0 L reactor and decomposed @ 27°C.

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

At equilibrium, there was 0.056 mol of Cl_2.

What is K_c?

$$[NOCl]_{initial}: \frac{1.0\ mol}{2.0\ L} = 0.50\ M$$

$$[Cl_2]_{eq} = \frac{0.056\ mol}{2\ L} = 0.028\ M$$

$$Q = \frac{(0)^2}{0.5} \qquad Q = 0$$

$$2NOCl_{(g)} \rightleftharpoons 2NO_{(g)} + Cl_2$$

I	0.50 M	0	0
C	$-2x$	$+2x$	$+x$
E	$0.500 - 2x$	$2 \cdot (0.028M) = 0.056M$	$0.028M$
	$0.44M$		

$$0 + x = 0.028M$$

$$x = "0.028M"$$

plug in eq. (c)

$$K_c = \frac{[NO]^2[Cl_2]^1}{[NOCl]^2}$$

$$K_c = \frac{(0.056)^2(0.028)}{(0.44)^2}$$

$$K_c = 4.5 \times 10^{-4}$$

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

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

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.?

$$Q = \frac{(3.00\times10^{-3})^2}{(2.00\times10^{-3})(2.00\times10^{-3})^3} \qquad Q = \frac{[NH_3]^2_{initial}}{[N_2]_{initial}[H_2]^3_{initial}}$$

$$Q = 5.6\times10^{7}$$

a) shift towards reactants to reach eq

b) what is the eq. concentration of each gas?

	$N_2(g)$	+	$3H_2(g)$	$\rightleftharpoons$	$2NH_3(g)$
I	2.00×10^{-3} M		2.00×10^{-3} M		3.00×10^{-2} M
C	$+x$		$+3x$		$-2x$
E					

which direction will the reaction shift to reach eq?

"Q" is before eq.

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

$$Q = \frac{[C]^c_{initial}\,[D]^d_{initial}}{[A]^a_{initial}\,[B]^b_{initial}}$$

when... $Q = K$ @ eq.

towards products $Q > K$

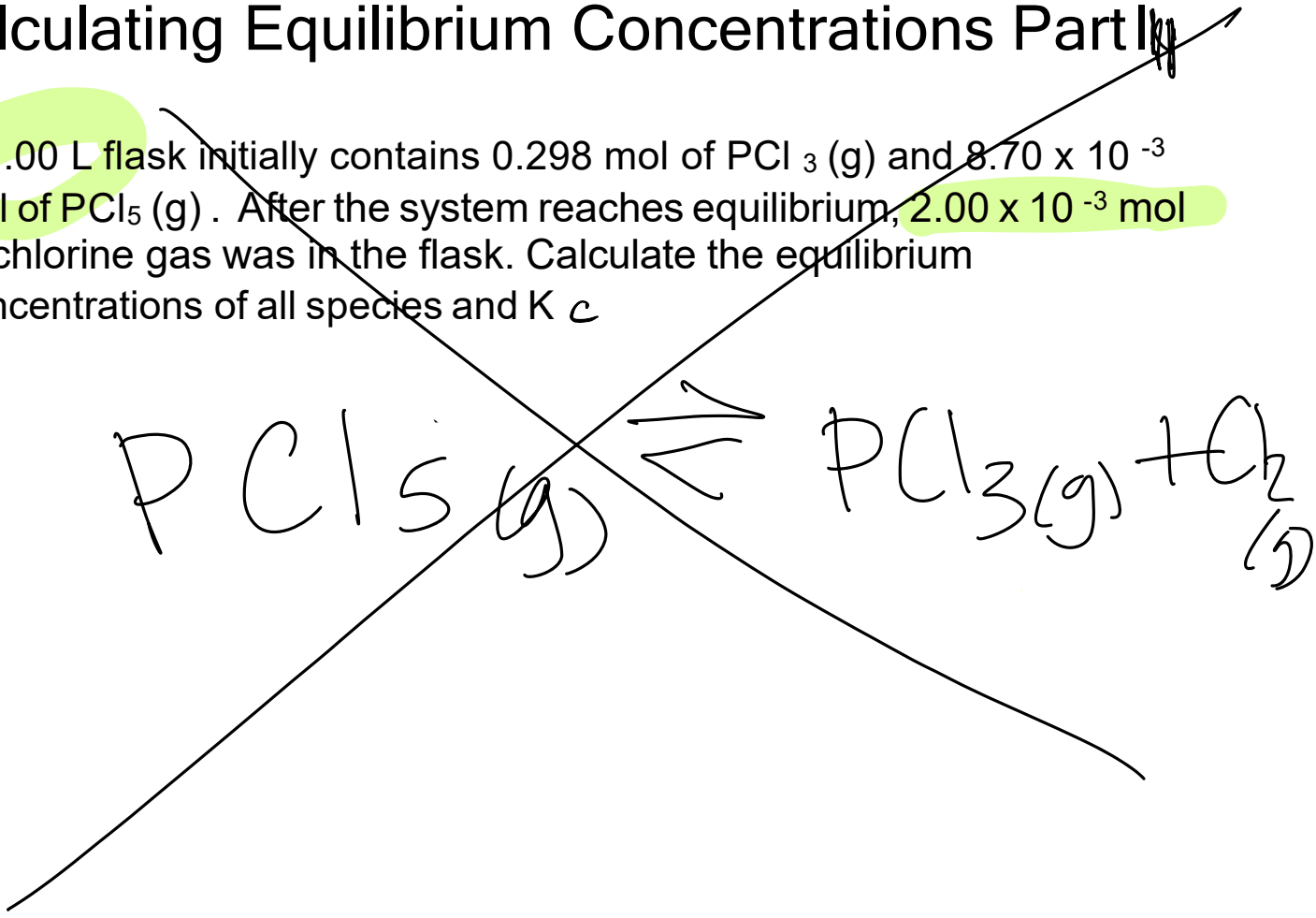
K_{eq} constant

K "half constant" towards reactants $Q < K$

$$K_{eq} = \frac{k_f}{k_r}$$

Calculating Equilibrium Concentrations Part II

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



Equilibrium Part III

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

at a certain temperature K_c is 0.0211. What is the equilibrium concentration of each gas if the initial concentration of PCl_5 is 1.00 M?

$Q = \frac{0}{1.0} = \emptyset$ $\emptyset < K$

make products to reach eq.

	$PCl_{5(g)}$	$\rightleftharpoons$	$PCl_{3(g)}$	$+ Cl_{2(g)}$
I	1.00 M		$\emptyset$	$\emptyset$
C	$-x$		$+x$	$+x$
E	$1.00 - x$		x	x

$$K_c = \frac{[PCl_3]^1[Cl_2]^1}{[PCl_5]^1}$$

$$0.0211 = \frac{(x)(x)}{1.00 - x}$$

method check

$\frac{1.00}{0.0211} = 47$ ∴ ✓

* if $\frac{[PCl_5]_{initial}}{K_c} \geq 100$ "change" is negligible

need to use quadratic formula

$$(1.00-x)\cdot 0.0211 = \frac{x^2}{1.00-x}\cdot(1.00-x)$$

$$0.0211 - 0.0211x = x^2$$

$$x^2 + 0.0211x - 0.0211 = 0$$

$a = 1$, $b = 0.0211$, $c = -0.0211$

$$x = \frac{-b \pm \sqrt{b^2-4ac}}{2a}$$

"x" = +0.135M

~~x = 0.135~~

~~x = -0.156~$$

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

	PCl_5	PCl_3	Cl_2
I	1.00 M	∅	∅
C	−x	+x	+x
E	1.00 − 0.135 = 0.865M	0.135M	0.135M

$[PCl_5] = 0.865M$

$[PCl_3] = 0.135M$

$[Cl_2] = 0.135M$

Example using "x is negligible"

For the reaction of acetic acid and water (equation given:)

$$HC_2H_3O_{2(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + C_2H_3O_{2(aq)}^-$$

the $K_c = 1.8 \times 10^{-5}$.

If the initial concentration of acetic acid ($HC_2H_3O_2$) is 1.00 M what are the equilibrium concentrations of all species?

$[HC_2H_3O_2]/K_c = \frac{1.00}{1.8 \times 10^{-5}} \sim 56{,}000$

can ignore "$-x$" for acetic acid

$HC_2H_3O_2(aq) + H_2O(l) \rightleftharpoons H_3O^+_{aq} + C_2H_3O_2^-$

	$HC_2H_3O_2$		H_3O^+	$C_2H_3O_2^-$
I	1.0 M		0	0
C	$-x$	negligible	$+x$	$+x$
E	1.0 M		$+x$	$+x$

$$K_c = \frac{[H_3O^+][C_2H_3O_2^-]}{[HC_2H_3O_2]}$$

$$K_c = \frac{x^2}{1.00} \qquad 1.8\times10^{-5} = \frac{x^2}{1}$$

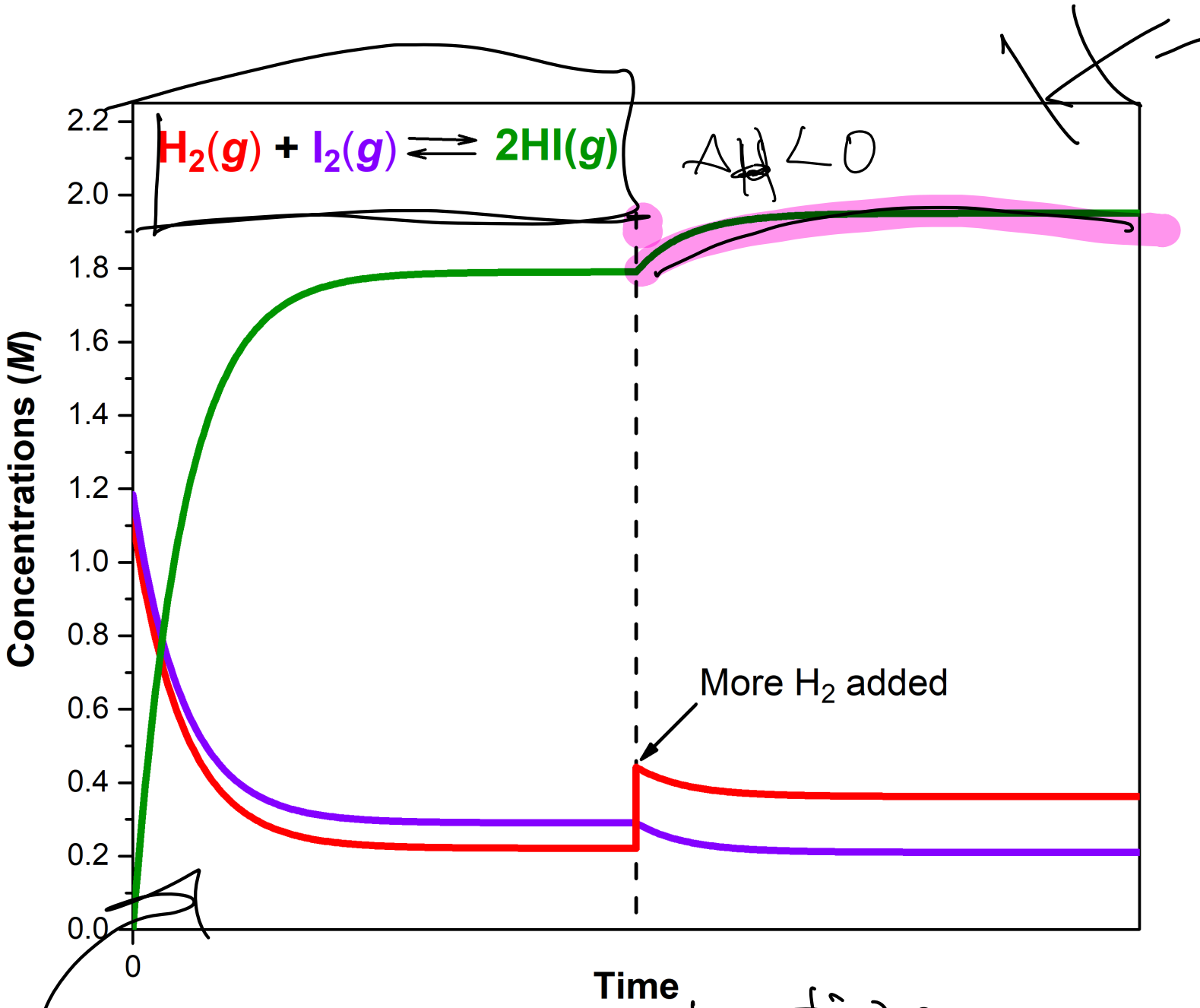
$$x = \sqrt{1.8\times10^{-5}\cdot 1} = x$$

$$x = 4.24\times10^{-3}$$

$[HC_2H_3O_2] = 1.0\ M$

$[H_3O^+]$ & $[C_2H_3O_2^-] = 4.2\times10^{-3}\ M$

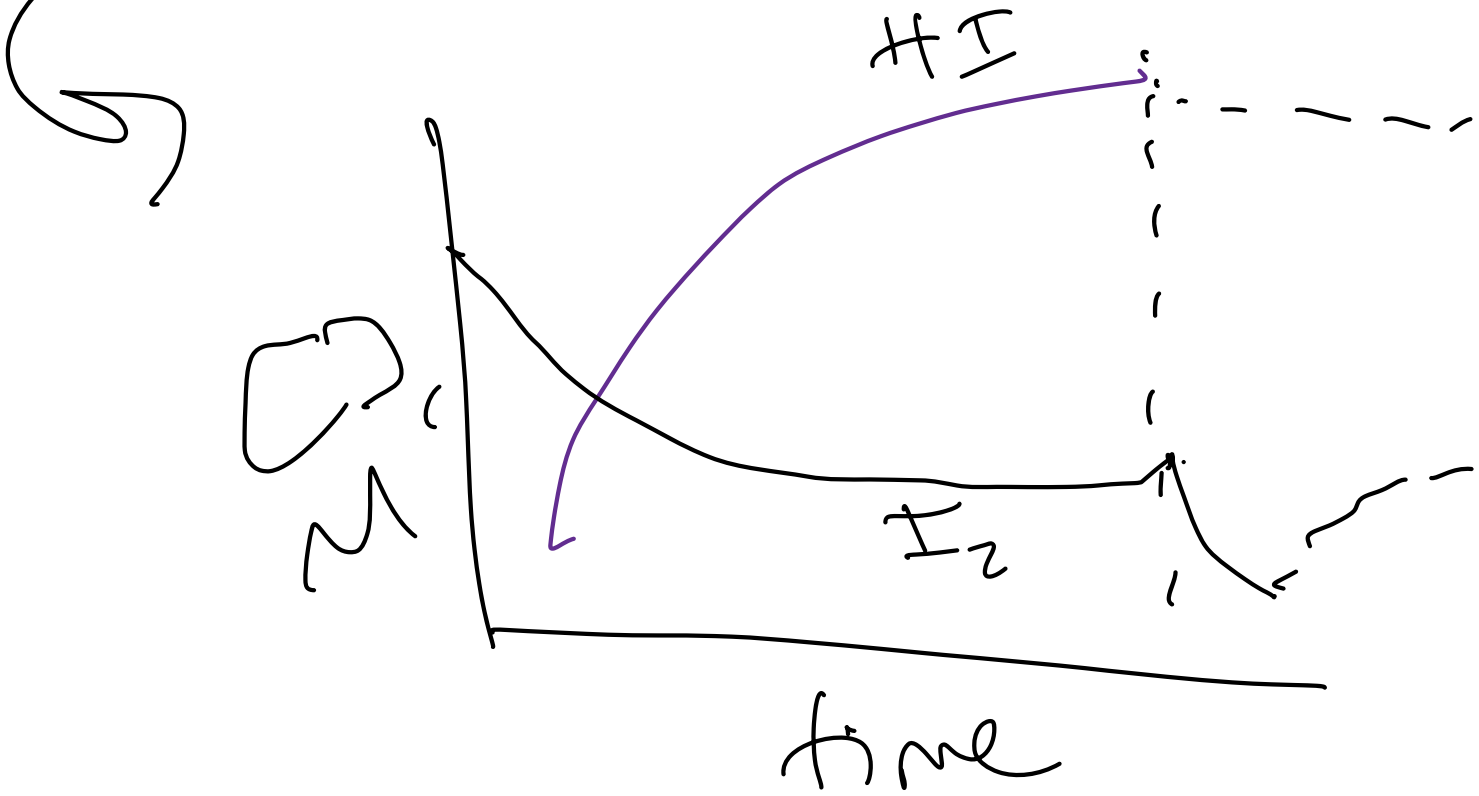
Le Chatelier's Principle



concentration

↑ [H2] shift to products

↓ [I2] shift to reactants


HI
I_2
time

Le Chateliers Principle Examples

Concentration

↑[H2] shift to products

↓[H2] shift to reactants

PV=nRT

P = 1/V

pressure or volume

↑ pressure shift to the side the least number of moles of gas

↓ pressure shift to the side with the most moles of gas

temperature

no change bc moles of gas of reactants = moles of gas of products side

4th

2nd

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

$PV = nRT$

$K = 1 \times 10^{-2}$

↓ pressure
shift ← reactants

$$Q = \frac{(P_{NH_3})^2}{P_{N_2} P_{H_2}^3}$$

$$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$$

$\Delta H < 0$

exothermic

$$H_{2(g)} + I_{2(g)} \underset{k_r}{\overset{k_f}{\rightleftharpoons}} 2HI_{(g)} + \text{heat}$$

↑ Temp
↑ rate constant

↓ temp
↓ rate constant

- add heat
shift reactant side

$$K_{eq} = \frac{k_f}{k_r}$$

$$K_{eq} = \frac{1}{10}$$

so new K_{eq} is smaller

$= 1$

- remove heat
shift to products

$K = \frac{k_f}{k_r} = 1$

$K_{eq} = \frac{10}{1}$

so new K_{eq} larger

exothermic

$A \underset{k_r}{\overset{k_f}{\rightleftharpoons}} B + \text{heat}$

↑ temp ↓ K — b/c k_r increase

↓ temp ↑ K — b/c k_f increased

endothermic

$\text{heat} + A \underset{k_r}{\overset{k_f}{\rightleftharpoons}} B$

↑ temp ↑ K — b/c k_f increase

↓ temp ↓ K — b/c k_r increase