

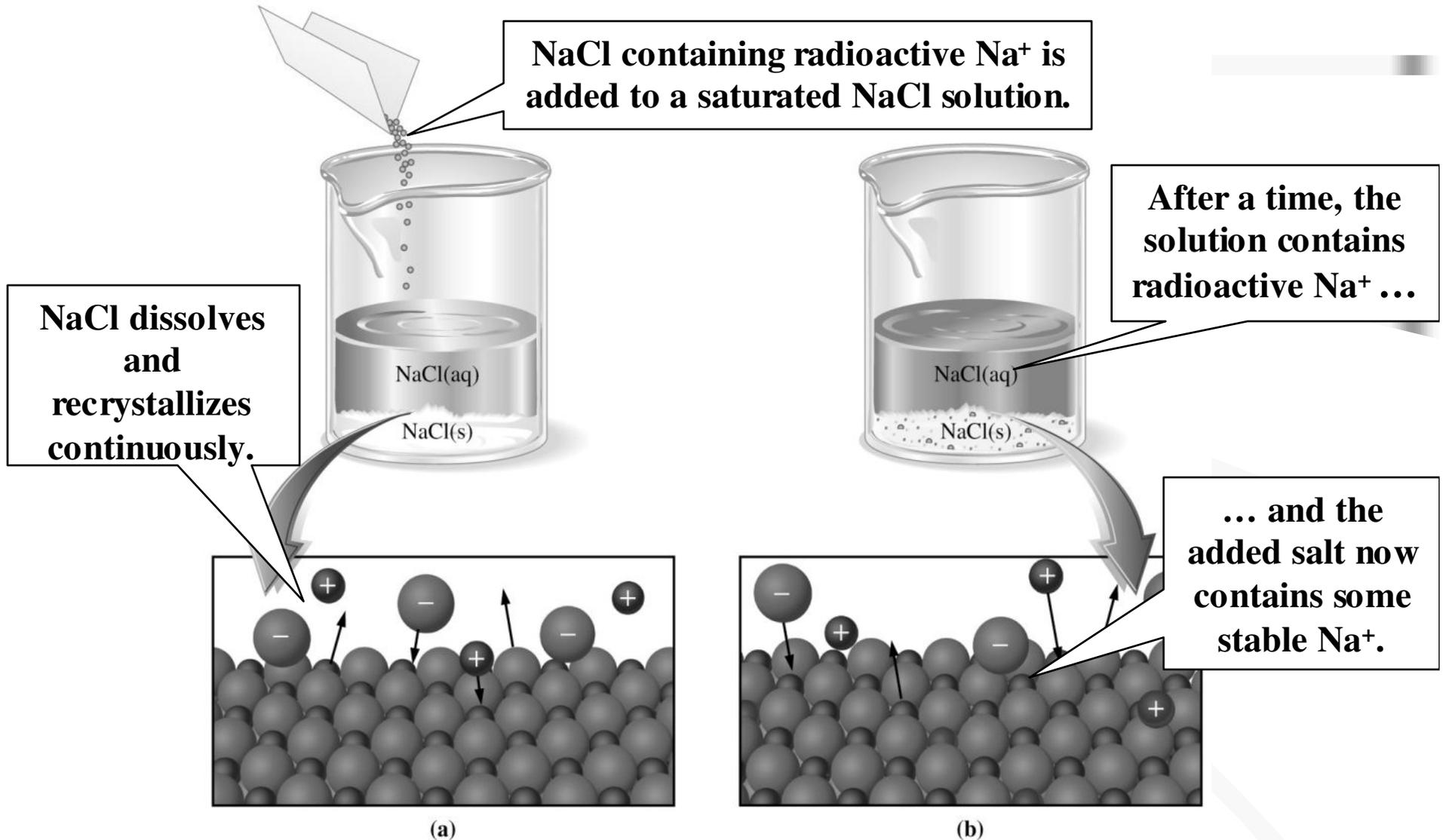
*Professor K*

Equilibria

# *Equilibria*

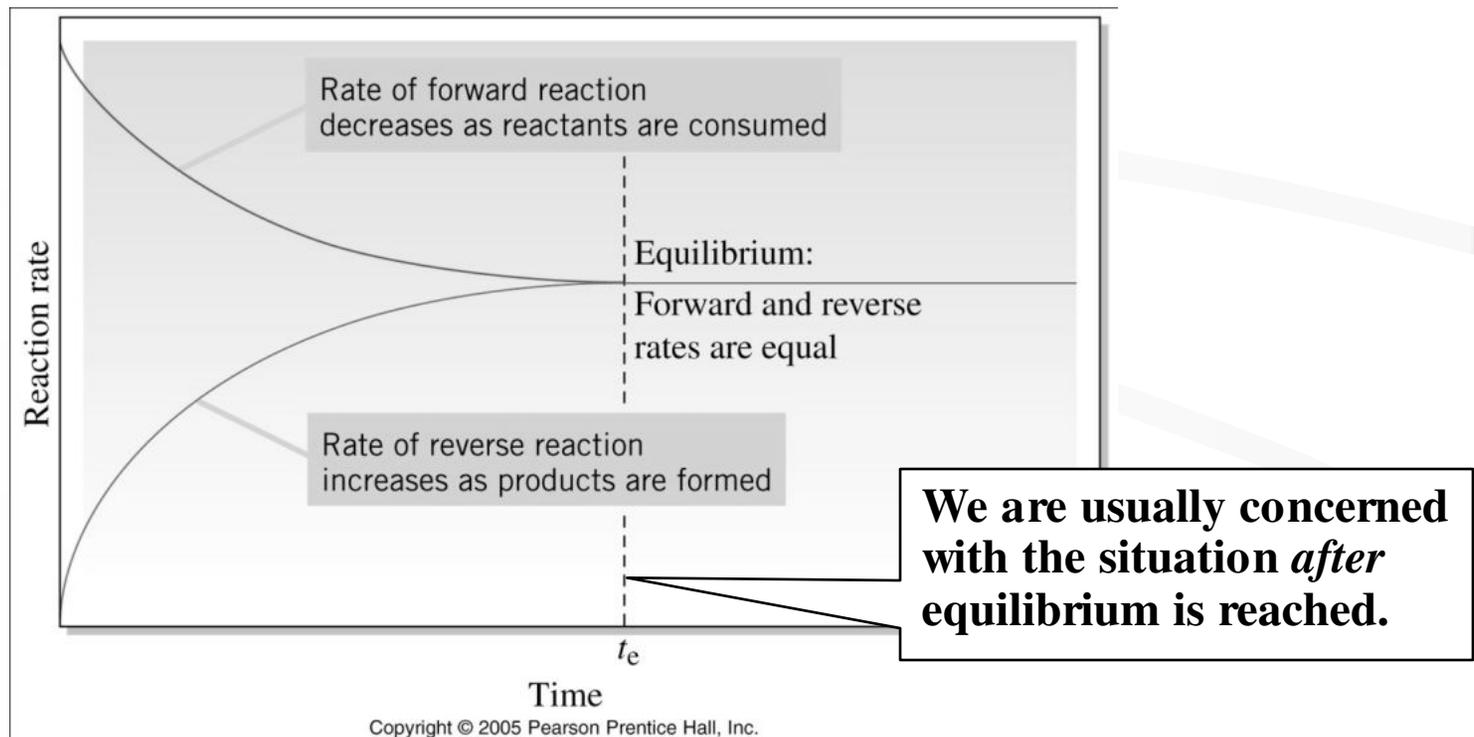
- We have mentioned the dynamic nature of a reaction at equilibrium several times before, and now explore the topic in detail
  - In an equilibrium, the forward and reverse processes are occurring at the same rate
  - Reactant and product concentrations are constant
  - The dynamic nature of an equilibrium (eq) can be demonstrated using radioactive tracers (why?)

# *Dynamic eq. illustrated*



# *Dynamic nature of equilibrium*

When a system reaches **equilibrium**, the forward and reverse reactions continue to occur ... but at equal rates.



After equilibrium the concentrations of reactants and products remain constant.

**Table 14.1 Three Experiments Involving the Reaction  $2 \text{HI}(\text{g}) \rightleftharpoons \text{H}_2(\text{g}) + \text{I}_2(\text{g})$  at 698 K**

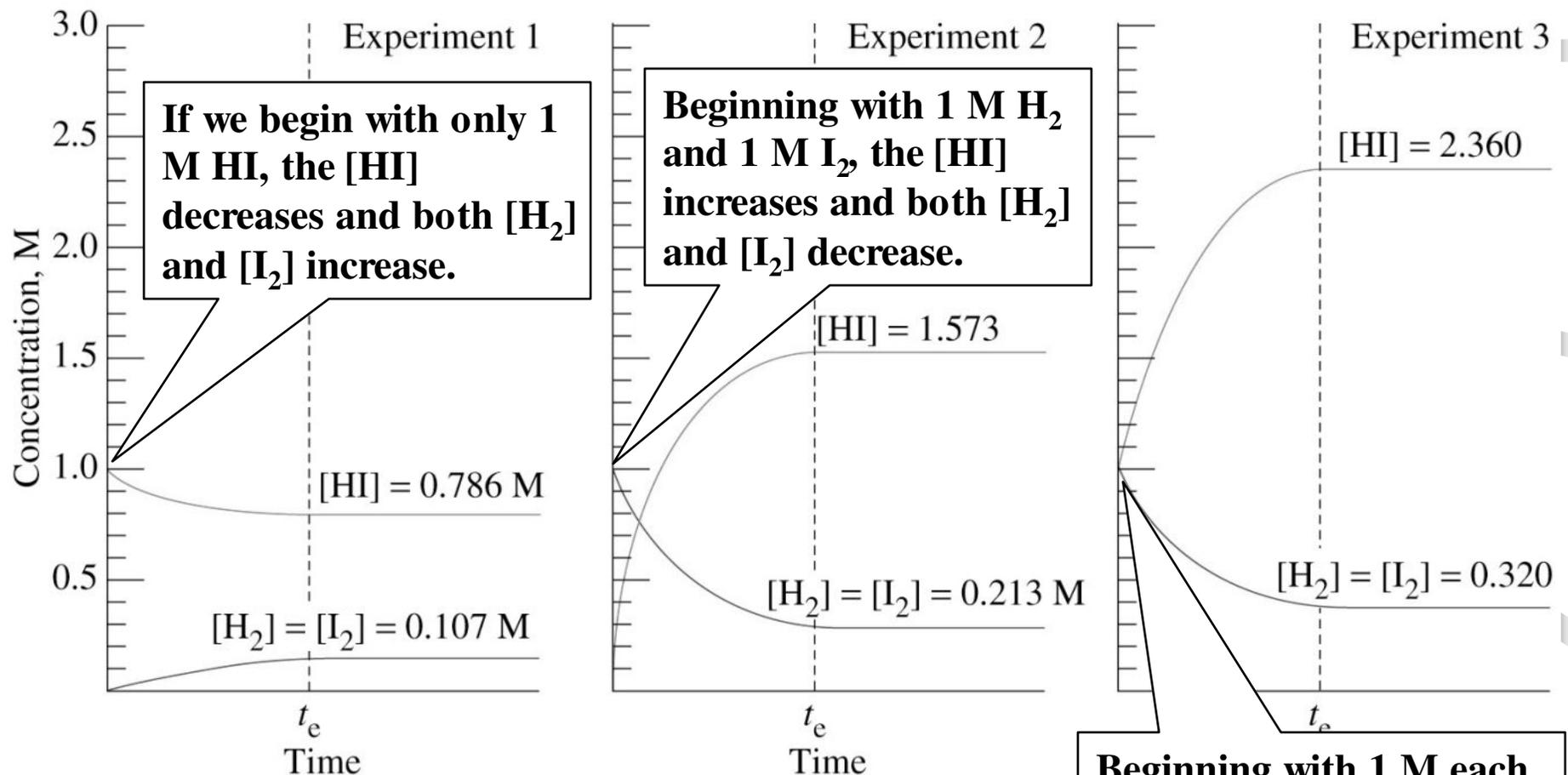
Experiment Number	Initial Concentrations, M	Equilibrium Concentrations, M	$\frac{[\text{H}_2][\text{I}_2]}{[\text{HI}]}$	$\frac{[\text{H}_2][\text{I}_2]}{2 [\text{HI}]}$	$\frac{[\text{H}_2][\text{I}_2]}{[\text{HI}]^2}$
1	[HI]: 1.000 [H <sub>2</sub> ]: 0.000 [I <sub>2</sub> ]: 0.000	0.786 0.107 0.107	0.0146	0.00728	0.0185
2	[HI]: 0.000 [H <sub>2</sub> ]: 1.000 [I <sub>2</sub> ]: 1.000	1.573 0.213 0.213	0.0288	0.0144	0.0183
3	[HI]: 1.000 [H <sub>2</sub> ]: 1.000 [I <sub>2</sub> ]: 1.000	2.360 0.320 0.320	0.0434	0.0217	0.0184

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**Regardless of the starting concentrations; once equilibrium is reached ...**

**... the expression with products in numerator, reactants in denominator, where each concentration is raised to the power of its coefficient, appears to give a constant.**

# Concentration vs. time



If we begin with only 1 M HI, the [HI] decreases and both [H<sub>2</sub>] and [I<sub>2</sub>] increase.

Beginning with 1 M H<sub>2</sub> and 1 M I<sub>2</sub>, the [HI] increases and both [H<sub>2</sub>] and [I<sub>2</sub>] decrease.

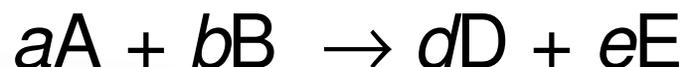
Beginning with 1 M each of H<sub>2</sub>, I<sub>2</sub>, and HI, the [HI] increases and both [H<sub>2</sub>] and [I<sub>2</sub>] decrease.

# *Equilibrium constants*

- Product concentrations divided by reactant concentrations gives the EQUILIBRIUM CONSTANT EXPRESSION or equation
- Ex: for  $2 \text{NO}(g) + \text{O}_2(g) \rightleftharpoons 2 \text{NO}_2(g)$ ,  
 $K_c = [\text{NO}_2]^2 / [\text{NO}]^2 [\text{O}_2] = 4.67 \times 10^{13}$
- Exponents equal the stoichiometric coefficients
- Given some of the variables, you can solve for the missing one

# *The equilibrium constant expression*

For the general reaction:



The equilibrium expression is:

$$K_c = \frac{[D]^d[E]^e}{[A]^a[B]^b}$$

**Each concentration is simply raised to the power of its coefficient**

***Products* in numerator.**

***Reactants* in denominator.**

## *Reaction rates at equilibrium*

- For the previous reaction, the forward rate =  $k_f[\text{NO}]^2 [\text{O}_2]$  where  $k$  is the rate
- The reverse rate =  $k_r[\text{NO}_2]^2$
- At eq, forward rate = reverse rate
- So, the equilibrium constant  $K_{\text{eq}} = k_f / k_r$
- Effect of reversing equation or multiplying whole system by a number
- For multi-step reactions, the overall rate depends only upon the slow step

# *The condition of equilibrium*

- The kinetics view:

$$K_c = (\text{forward rate})/(\text{reverse rate}) = k_f/k_r$$

- The thermodynamics view:
  - The equilibrium constant can be related to other fundamental thermodynamic properties and is called the ***thermodynamic equilibrium constant***,  $K_{\text{eq}}$ .
  - The thermodynamic equilibrium constant expression uses dimensionless quantities known as ***activities*** in place of molar concentrations.
  - We will not focus on this topic in any detail

## *Modifying the chemical eq.*

Consider the reaction:  $2 \text{NO}(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2 \text{NO}_2(\text{g})$

$$K_c = \frac{[\text{NO}_2]^2}{[\text{NO}]^2 [\text{O}_2]} = 4.67 \times 10^{13} \text{ (at 298 K)}$$

Now consider the reaction:  $2 \text{NO}_2(\text{g}) \rightleftharpoons 2 \text{NO}(\text{g}) + \text{O}_2(\text{g})$

What will be the equilibrium constant  $K'_c$  for the new reaction?

$$K'_c = \frac{[\text{NO}]^2 [\text{O}_2]}{[\text{NO}_2]^2} = \frac{1}{\frac{[\text{NO}_2]^2}{[\text{NO}]^2 [\text{O}_2]}} = \frac{1}{K_c} = \frac{1}{4.67 \times 10^{13}} = 2.14 \times 10^{-14}$$

## *Modifying the chemical eq. (cont'd)*

Consider the reaction:  $2 \text{NO}(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2 \text{NO}_2(\text{g})$

$$K_c = \frac{[\text{NO}_2]^2}{[\text{NO}]^2 [\text{O}_2]} = 4.67 \times 10^{13} \text{ (at 298 K)}$$

Now consider the reaction:  $\text{NO}_2(\text{g}) \rightleftharpoons \text{NO}(\text{g}) + \frac{1}{2} \text{O}_2(\text{g})$

What will be the equilibrium constant  $K''_c$  for the new reaction?

$$K''_c = \frac{[\text{NO}] [\text{O}_2]^{1/2}}{[\text{NO}_2]} = \left[ \frac{1}{K_c} \right]^{1/2} = \sqrt{2.14 \times 10^{-14}} = 1.46 \times 10^{-7}$$

## *Modifying the chemical eq. – summary*

- For the reverse reaction,  $K$  is the ***reciprocal*** of  $K$  for the forward reaction.
- When an equation is divided by two,  $K$  for the new reaction is the ***square root*** of  $K$  for the original reaction.
- General rule:
  - *When the coefficients of an equation are multiplied by a common factor  $n$  to produce a new equation, we raise the original  $K_c$  value to the power  $n$  to obtain the new equilibrium constant.*
- It should be clear that *we must write a balanced chemical equation when citing a value for  $K_c$ .*

# *The equilibrium constant for an overall reaction*

Suppose we need:  $\text{N}_2\text{O}(\text{g}) + 3/2 \text{O}_2(\text{g}) \rightleftharpoons 2 \text{NO}_2(\text{g}) \quad K_c(1) = ??$

and we're given:



- **Adding** the given equations gives the desired equation.
- **Multiplying** the given values of  $K$  gives the equilibrium constant for the overall reaction.
- (To see why this is so, write the equilibrium constant expressions for the two given equations, and multiply them together. Examine the result ...)

# *Reaction rates at equilibrium*

## *(cont'd)*

- Partial pressures can be used in place of concentrations for gas equations
- Pure solids and liquids DO NOT appear in equilibrium constant expressions since their CONCENTRATIONS don't change during the reactions (AMOUNTS of course change, but not concentrations)
- Extreme values for K indicate non-reversible reactions



~~$$K_c = \frac{[\text{CaO}] [\text{CO}_2]}{[\text{CaCO}_3]}$$~~

$$K_c = [\text{CO}_2]$$

# *Equilibrium constants– when do we need them, and when do we not?*

- A very **large** numerical value of  $K_c$  or  $K_p$  signifies that a reaction goes (essentially) to completion.
- A very **small** numerical value of  $K_c$  or  $K_p$  signifies that the forward reaction, as written, occurs only to a slight extent.
- An equilibrium constant expression applies only to a reversible reaction **at equilibrium**.
- Although a reaction may be *thermodynamically favored*, it may be *kinetically controlled* ...
- Thermodynamics tells us “it’s possible (or not)”
- Kinetics tells us “it’s practical (or not)”

# *Equilibria involving gases*

- In reactions involving gases, it is often convenient to measure partial pressures rather than molarities.
- In these cases, a ***partial pressure equilibrium constant***,  $K_p$ , is used.

$$K_p = \frac{(P_G)^g (P_H)^h}{(P_A)^a (P_B)^b}$$

$K_c$  and  $K_p$  are related by:  $K_p = K_c (RT)^{\Delta n(gas)}$

*where  $\Delta n(gas)$  is the change in number of moles of gas as the reaction occurs in the forward direction.*

$\Delta n(gas) = \text{mol gaseous products} - \text{mol gaseous reactants}$

# *Reaction quotient*

- An examination of the K type for a reaction NOT at eq
- For **nonequilibrium** conditions, the expression having the same form as  $K_c$  or  $K_p$  is called the **reaction quotient,  $Q_c$  or  $Q_p$** .
- The reaction quotient is not constant for a reaction, but is useful for *predicting the direction* in which a net change must occur to establish equilibrium.
- To determine the direction of net change, we compare the magnitude of  $Q_c$  to that of  $K_c$ .

# Q (cont'd)

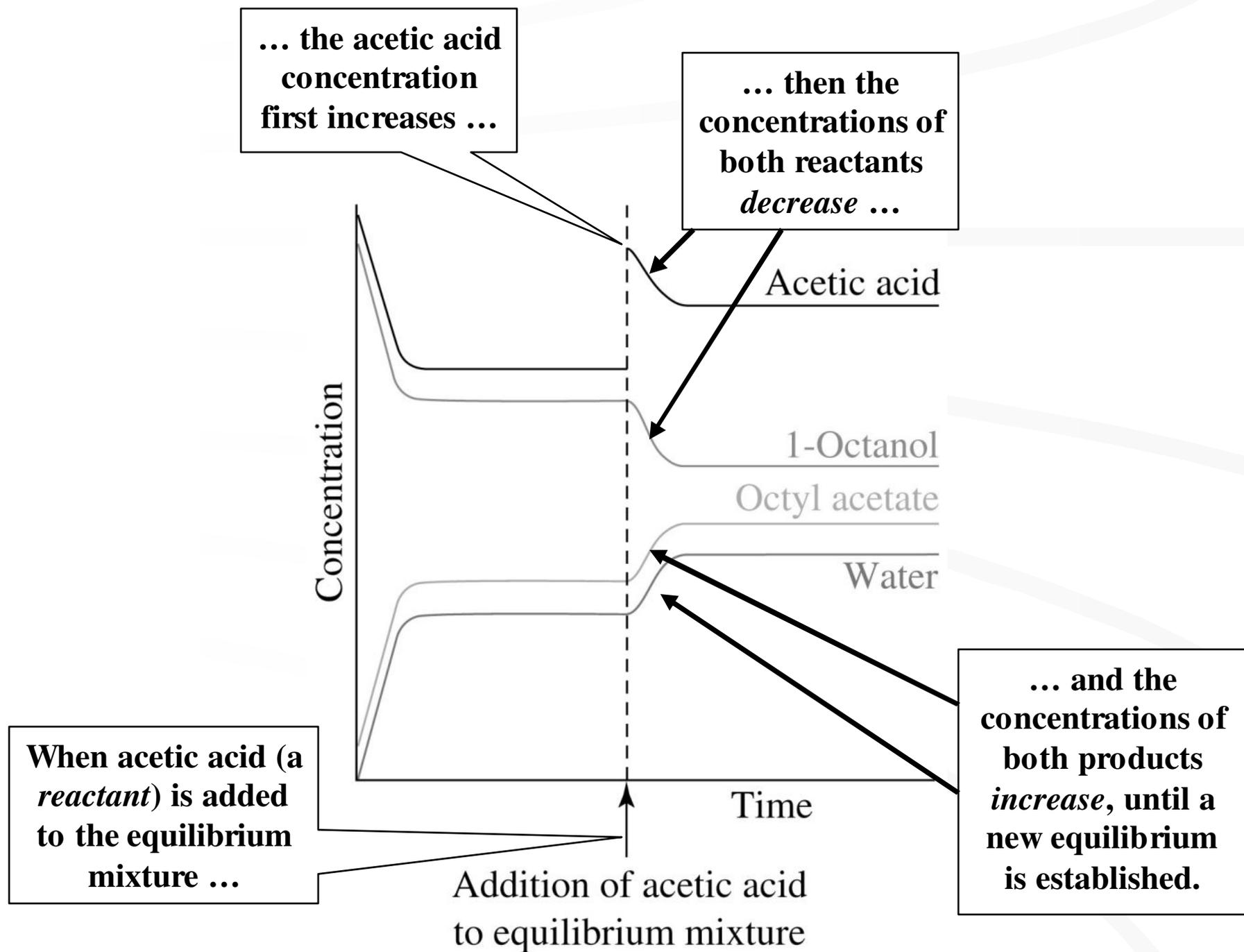
			Initial state	Net change
<p>When <math>Q</math> is <i>smaller</i> than <math>K</math>, the denominator of <math>Q</math> is too big; we have “too much reactants.”</p>		$Q = \frac{\text{---}}{\text{reactants}} = 0$	Pure reactants	$\rightarrow$ (forms products)
		$Q = \frac{\text{products}}{\text{reactants}} < K$	Mostly reactants	$\rightarrow$ (forms products)
<p>When <math>Q = K</math>, equilibrium has been reached.</p>		$Q = \frac{\text{products}}{\text{reactants}} = K$	At equilibrium	$\rightleftharpoons$ (none)
<p>When <math>Q</math> is <i>larger</i> than <math>K</math>, the numerator of <math>Q</math> is too big; we have “too much products.”</p>		$Q = \frac{\text{products}}{\text{reactants}} > K$	Mostly products	(forms reactants) $\leftarrow$
		$Q = \frac{\text{products}}{\text{---}} = \infty$	Pure products	(forms reactants) $\leftarrow$

# *LeChatelier's principle*

- A stress placed on a reaction system at equilibrium is minimized
- Addition of products or removal of products
- Changing pressure (4 slides ahead)
- Changing temperature
- Addition of catalyst
  - A common word very few understand...
  - Enzymes

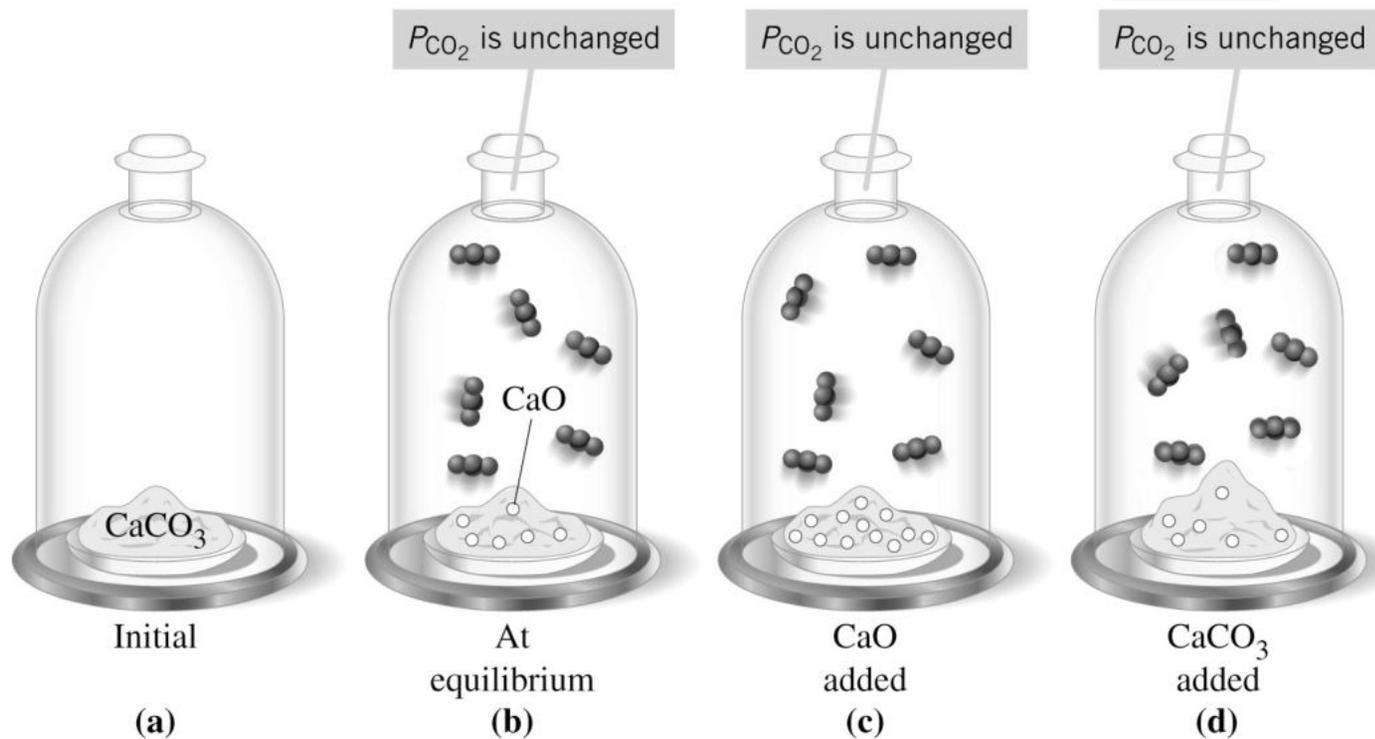
## *Changing the amounts of reacting species*

- At equilibrium,  $Q = K_c$ .
- If the concentration of one of the **reactants** is increased, the **denominator** of the reaction quotient increases.
- $Q$  is now **less than**  $K_c$ .
- This condition is only temporary, however, because the concentrations of all species must change in such a way so as to make  $Q = K_c$  again.
- In order to do this, the concentrations of the **products increase**; the reaction is shifted to the right.



# *Heterogeneous eq.* *and Le Chatelier's principle*

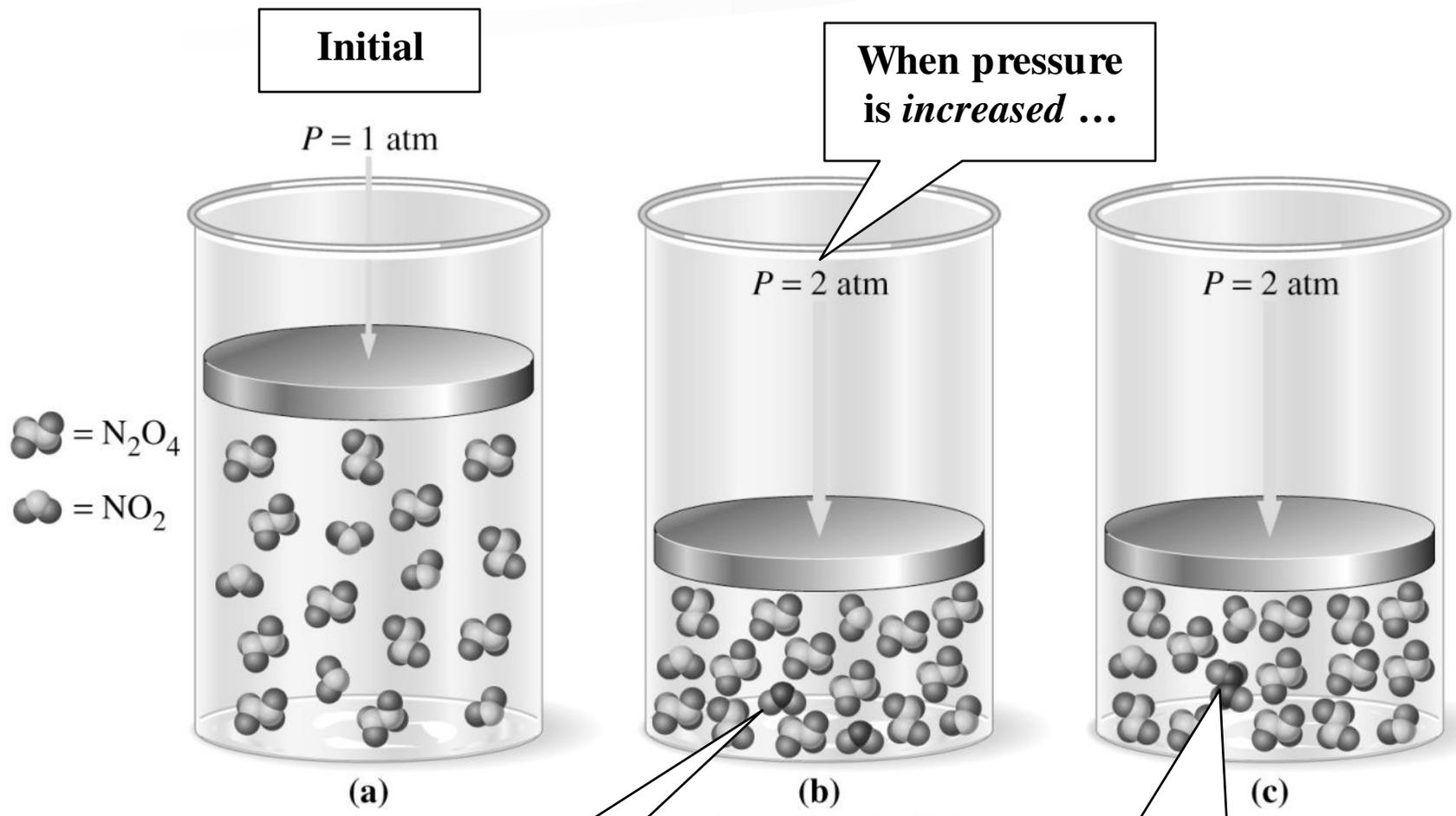
- Addition or removal of pure solids or pure liquids from a system at equilibrium does *not* affect the equilibrium.



## *Changing external $P$ or $V$ in gaseous eq*

- When the external pressure is **increased** (or system volume is reduced), a reaction shifts in the direction producing the **smaller** number of moles of gas.
- When the external pressure is **decreased** (or the system volume is increased), a reaction shifts in the direction producing the **larger** number of moles of gas.
- If there is no change in the number of moles of gas in a reaction, changes in external pressure (or system volume) have no effect on an equilibrium.

Example:  $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2 \text{HI}(\text{g})$  equilibrium is unaffected by pressure changes.



... *two* molecules of  $\text{NO}_2$  combine ...

... to give *one* molecule of  $\text{N}_2\text{O}_4$ , reducing the pressure increase.

# *T changes and catalysis*

- Raising the temperature of an equilibrium mixture shifts equilibrium in the direction of the endothermic reaction; lowering the temperature shifts equilibrium in the direction of the exothermic reaction.
  - Consider heat as though it is a product of an exothermic reaction or as a reactant of an endothermic reaction, and apply Le Châtelier's principle.
- A catalyst lowers the activation energy ... of both the forward and the reverse reaction.
- Adding a catalyst does not affect an equilibrium state.
- A catalyst merely causes equilibrium to be achieved faster.

# *Determining values of eq constants experimentally*

- When initial amounts of one or more species, and equilibrium amounts of one or more species, are given, the amounts of the remaining species in the equilibrium state and, therefore, the equilibrium concentrations often can be established.
- A useful general approach is to tabulate under the chemical equation:
  - the concentrations of substances present initially
  - changes in these concentrations that occur in reaching equilibrium
  - the equilibrium concentrations.
- This sort of table is sometimes called an “ICE” table: Initial/Change/Equilibrium.

## *Calculating eq quantities from $K_c$ and $K_p$ values*

- When starting with initial reactants and no products and with the known value of the equilibrium constant, these data are used to calculate the amount of substances present at equilibrium.
- Typically, an ICE table is constructed, and the symbol  $x$  is used to identify one of the changes in concentration that occurs in establishing equilibrium.
- Then, all the other concentration changes are related to  $x$ , the appropriate terms are substituted into the equilibrium constant expression, and the equation solved for  $x$ .