

## Review Exam 3

### Chapters

14

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## Review Chap 14: CHEMICAL KINETICS

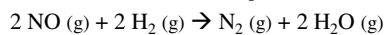
### CHEMICAL KINETICS DEALS WITH

1. How **FAST** {Speed like miles per hour  
and
2. By what **MECHANISM** Does a  
Reaction Take Place ?

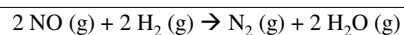
Given the following data, determine the rate law for the all gas reaction of nitrogen monoxide reacting with hydrogen forming nitrogen and water

Experiment	moles NO	moles H <sub>2</sub>	Initial Rate (M/s)
1	0.10	0.10	1.23 x 10 <sup>-3</sup>
2	0.10	0.20	2.46 x 10 <sup>-3</sup>
3	0.20	0.10	4.92 x 10 <sup>-3</sup>

Write, balance, and interpret reaction



$$\text{Rate} \propto [\text{NO}]^x [\text{H}_2]^y$$



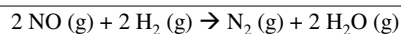
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3	0.20	0.10	4.92 x 10 <sup>-3</sup>

From Exp 1 & 2

When [H<sub>2</sub>] doubles, Rate doubles

$$\text{Rate} \propto [\text{H}_2]^1 \leftarrow$$



$$\text{Rate} \propto [\text{NO}]^x [\text{H}_2]^y$$

Experiment	moles NO	moles H <sub>2</sub>	Initial Rate (M/s)
1	0.10	0.10	1.23 x 10 <sup>-3</sup>
2	0.10	0.20	2.46 x 10 <sup>-3</sup>
3	0.20	0.10	4.92 x 10 <sup>-3</sup>

From Exp 2 & 3

When [NO] doubles, Rate quadruples

$$\text{Rate} \propto [\text{NO}]^2 \leftarrow$$

$$\text{rate} = k [\text{NO}]^2 [\text{H}_2]$$

1<sup>st</sup> order w.r.t H<sub>2</sub>

2<sup>nd</sup> order w.r.t. NO

3<sup>rd</sup> order overall

k is the rate constant.

## TEMPERATURE and RATE

- As temperature increases so does the reaction rate
- The rate constant ( $k$ ) is temperature dependent
- The rule of thumb is: rate doubles for each 10 degree rise in temp

## Half-life $\{t_{1/2}\}$

is defined as the time required for one-half of a reactant to react

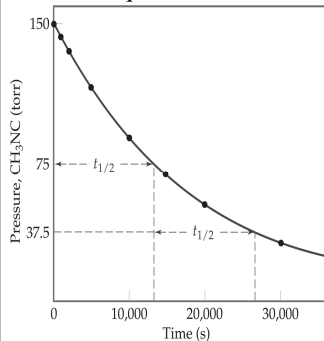
For  $A \rightarrow B$

at  $t_{1/2}$ ,

the concentration of A is one-half the initial concentration of A

## HALF-LIFE

time required for one-half of a reactant to react



Pressure of  $\text{CH}_3\text{NC}$  is  $\frac{1}{2}$  of the original Pressure at  $t_{1/2}$

In this example

at 13,000 sec  
 $P_{\text{CH}_3\text{NC}} = 0.5 P_0$   
 $= 75 \text{ torr}$

All radioactive decay is 1<sup>st</sup> order

$$\ln \frac{[A]_0}{[A]} = k t$$

At  $t_{1/2}$  concentration is  $\frac{1}{2}$  initial

$$\ln \frac{[A]_0}{[\frac{1}{2}A]_0} = k t_{1/2}$$

$$\ln 2 = k t_{1/2}$$

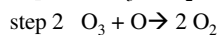
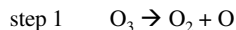
In a chemical reaction bonds are broken & bonds are formed

- The sequence of events that describes the actual process by which reactants become products is called the reaction mechanism.
- The mechanism MUST agree with experiment

Reaction mechanisms

- Reactions occur through several discrete steps
- Each of these is known as an elementary reaction or elementary process
- The molecularity of a process tells how many molecules are involved in the process

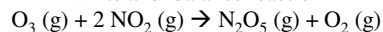
It has been proposed that the mechanism of  
 $2 \text{O}_3 \rightarrow 3 \text{O}_2$   
 proceeds by the following mechanism



- |  |                          |
|--|--------------------------|
| (a) Describe the molecularity of each elementary reaction in this mechanism. | 1. 1 <sup>st</sup> order |
| (b) Does mechanism agree with balanced reaction?                             | 2. 2 <sup>nd</sup> order |
| (c) Identify the intermediate(s).  | (b)                      |
|  | Yes                      |
|  | (c)                      |
|  | O                        |

Ozone reacts with nitrogen dioxide to produce dinitrogen pentoxide and oxygen

Write and balance reaction



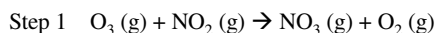
The experimental rate law is

$$\text{rate} = k[\text{O}_3][\text{NO}_2]$$

Interpret results

1<sup>st</sup> order with respect to Ozone & nitrogen dioxide

The proposed mechanism for the reaction of Ozone with Nitrogen dioxide is



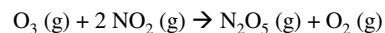
Does the proposed mechanism agree with experiment?

Yes, steps add to give  $\text{O}_3 + 2 \text{NO}_2 \rightarrow \text{N}_2\text{O}_5 + \text{O}_2$

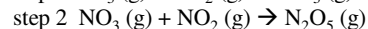
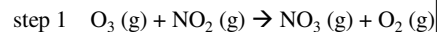
What is the intermediate?



What can be said about the relative rates of the two steps of the mechanism?



Mechanism



The experimental rate law is  $\text{rate} = k[\text{O}_3][\text{NO}_2]$

Because the rate law conforms to the molecularity of the first step, that must be the rate-determining step.

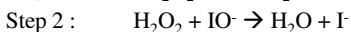
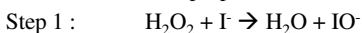
The second step must be much faster than the first one.

The decomposition of Hydrogen Peroxide  
 $2 \text{H}_2\text{O}_2 (\text{aq}) \rightarrow 2 \text{H}_2\text{O} (\text{liq}) + \text{O}_2 (\text{g})$   
 is catalyzed by iodide ion

By experiment the rate law is found to be

$$\text{Rate} = k[\text{H}_2\text{O}_2][\text{I}^-]$$

The proposed mechanism



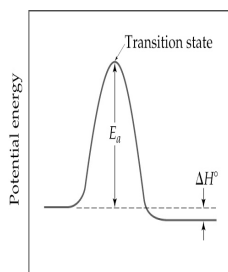
Is this an acceptable mechanism ?

yes

## THE COLLISION THEORY (Three parts)

1. Molecules can only react if they collide
2. collide with sufficient energy\*.  
**\*Activation Energy ( $E_a$ ):** The energy barrier that must be surmounted before reactants can be converted to products.
3. correctly oriented molecules

Figure 14.15  
Not all collisions lead to products



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### Arrhenius Equation

Svante Arrhenius developed a mathematical relationship between  $k$  and  $E_a$ :

$$k = A e^{-\frac{E_a}{RT}}$$

Taking the natural logarithm of both sides, the equation becomes

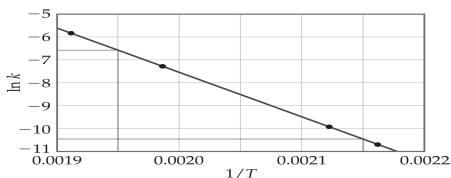
$$\ln k = -\frac{E_a}{R} \left(\frac{1}{T}\right) + \ln A$$

### Arrhenius Equation

$$\ln k = -\frac{E_a}{R} \left(\frac{1}{T}\right) + \ln A$$

$$y = m x + b$$

If  $k$  is determined experimentally at several temperatures,  $E_a$  can be calculated from the slope of a plot of  $\ln k$  vs.  $\frac{1}{T}$



### Chapter 15 Chemical Equilibrium

The reaction for the production of ammonia can be written in a number of ways

- (a)  $\text{N}_2(\text{g}) + 3 \text{H}_2(\text{g}) = 2 \text{NH}_3(\text{g})$
- (b)  $\frac{1}{2} \text{N}_2(\text{g}) + \frac{3}{2} \text{H}_2(\text{g}) = \text{NH}_3(\text{g})$
- (c)  $\frac{1}{3} \text{N}_2(\text{g}) + \text{H}_2(\text{g}) = \frac{2}{3} \text{NH}_3(\text{g})$

Write the equilibrium constant expressions and how they are related

- (a)  $\text{N}_2(\text{g}) + 3 \text{H}_2(\text{g}) = 2 \text{NH}_3(\text{g})$
- (b)  $\frac{1}{2} \text{N}_2(\text{g}) + \frac{3}{2} \text{H}_2(\text{g}) = \text{NH}_3(\text{g})$
- (c)  $\frac{1}{3} \text{N}_2(\text{g}) + \text{H}_2(\text{g}) = \frac{2}{3} \text{NH}_3(\text{g})$

$$K_a = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} \quad K_b = \frac{[\text{NH}_3]}{[\text{N}_2]^{1/2}[\text{H}_2]^{3/2}} \quad K_c = \frac{[\text{NH}_3]^{2/3}}{[\text{N}_2]^{1/3}[\text{H}_2]}$$

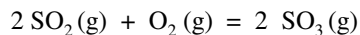
$$K_a = K_b^2 \quad K_a = K_c^3 \quad K_b^2 = K_c^3$$

### The Equilibrium Constant

The ratio of the rate constants is a constant at that temperature, and the expression becomes

$$K_{eq} = \frac{k_f}{k_r} = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]}$$

The **Initial Change Equilibrium** method is used to calculate equilibrium constant



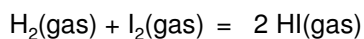
<b>Initial</b>	Moles	Moles	Moles
<b>Change</b>	-2x	-x	+ 2x
<b>Equilibrium</b>	Moles	Moles	Moles

Change to Concentrations at Equilibrium

What Does the Value of  $K$  Mean?

If  $K \gg 1$ , the reaction is *product-favored*; product predominates at equilibrium.

If  $K \ll 1$ , the reaction is *reactant-favored*; reactant predominates at equilibrium.



	$\text{H}_2$ , Moles	$\text{I}_2$ , Moles	$\text{HI}$ , Moles
<b>I</b> nitially	$1.000 \times 10^{-3}$	$2.000 \times 10^{-3}$	0
<b>C</b> hange	$-9.35 \times 10^{-4}$	$-9.35 \times 10^{-4}$	$+1.87 \times 10^{-3}$
<b>E</b> quilibrium	$6.5 \times 10^{-5}$	$1.065 \times 10^{-3}$	$1.87 \times 10^{-3}$

the equilibrium constant

$$K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]}$$

$$= \frac{(1.87 \times 10^{-3})^2}{(6.5 \times 10^{-5})(1.065 \times 10^{-3})}$$

$$= 51$$

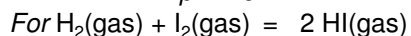
UNITS ?

Relationship between  $K_c$  and  $K_p$

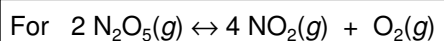
$$K_p = K_c (RT)^{\Delta n}$$

Where  $\Delta n =$  (moles of gaseous product)  
- (moles of gaseous reactant)

$$K_p = K_c$$



WHY ?



The  $K_p$  and  $K_c$  expressions :

$$K_p = (\text{P}_{\text{NO}_2})^4 (\text{P}_{\text{O}_2}) / (\text{P}_{\text{N}_2\text{O}_5})^2$$

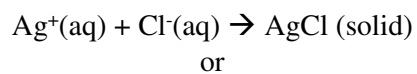
$$K_c = [\text{NO}_2]^4 [\text{O}_2] / [\text{N}_2\text{O}_5]^2$$

Is  $K_p = K_c$  ?

No !

## HETEROGENEOUS EQUILIBRIUM

Pure Solids and Liquids do not have a concentration therefore they do not appear in the equilibrium expression



$$K_c = 1 / [\text{Ag}^+(\text{aq})] [\text{Cl}^-(\text{aq})]$$

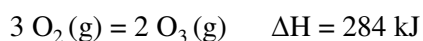
or

$$K_{sp} = [\text{Ag}^+(\text{aq})] [\text{Cl}^-(\text{aq})] = 1 / K_c$$

## Le Châtelier's Principle

### Le Châtelier's Principle

- The Effect of Changes in Pressure
- The Effect of Changes in Temperature
- Catalysts increase the rate of both the forward *and* reverse reactions. Equilibrium is achieved faster, but the equilibrium composition remains unaltered.



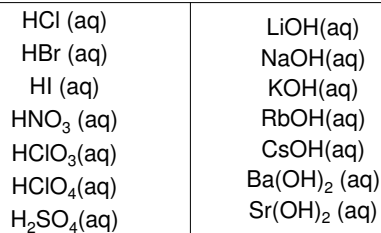
What would be the effect of

- (a) Decreasing the volume of the system
- (b) Increasing the pressure by adding  $\text{O}_2$
- (c) Decreasing the temperature
- (d) Adding a catalyst

### Chapter 16 Acids and Bases

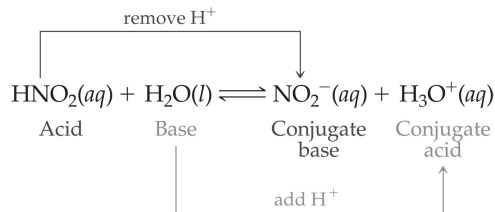
- **Arrhenius**
  - Acid: Hydronium ion ( $\text{H}_3\text{O}^+$ )
  - Base: Hydroxide ions ( $\text{OH}^-$ )
- **Brønsted–Lowry**
  - Acid: Proton donor
  - Base: Proton acceptor
- **Lewis**
  - Acid *electron-pair acceptor*
  - Base is an *electron-pair donor*

No Equilibrium for the 7 Strong Acids  
or 7 Strong Bases

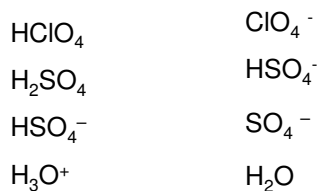


Conjugate Acids and Bases:

An Acid and a Base that differ only in the presence  
{or absence} of a proton.



What are the conjugate bases of the  
following Brønsted–Lowry acids



Which one of the conjugate bases of the  
following Brønsted–Lowry acids is incorrect?

- (a) ClO<sup>-</sup> for HClO
- (b) HS<sup>-</sup> for H<sub>2</sub>S
- (c) NH<sub>3</sub> for NH<sub>4</sub><sup>+</sup>
- (d) SO<sub>4</sub><sup>2-</sup> for HSO<sub>4</sub><sup>-</sup>
- (e) H<sub>2</sub>SO<sub>4</sub> for HSO<sub>4</sub><sup>-</sup>

Ion-Product Constant

This special equilibrium constant is referred to as  
the ion-product constant for water,  $K_w$

$$K_w = [\text{H}_3\text{O}^+] [\text{OH}^-]$$

At 25 °C,  $K_w = 1.0 \times 10^{-14}$

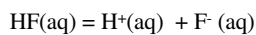
pH is defined as

$$\text{pH} = -\log [\text{H}_3\text{O}^+]$$

	[H <sup>+</sup> ] (M)	pH	pOH	[OH <sup>-</sup> ] (M)
	1 (1×10 <sup>-0</sup> )	0.0	14.0	1×10 <sup>-14</sup>
	1×10 <sup>-1</sup>	1.0	13.0	1×10 <sup>-13</sup>
Gastric juice	1×10 <sup>-2</sup>	2.0	12.0	1×10 <sup>-12</sup>
Lemon juice	1×10 <sup>-3</sup>	3.0	11.0	1×10 <sup>-11</sup>
Cola, vinegar	1×10 <sup>-4</sup>	4.0	10.0	1×10 <sup>-10</sup>
Wine	1×10 <sup>-5</sup>	5.0	9.0	1×10 <sup>-9</sup>
Tomatoes	1×10 <sup>-6</sup>	6.0	8.0	1×10 <sup>-8</sup>
Banana	1×10 <sup>-7</sup>	7.0	7.0	1×10 <sup>-7</sup>
Black coffee	1×10 <sup>-8</sup>	8.0	6.0	1×10 <sup>-6</sup>
Rain	1×10 <sup>-9</sup>	9.0	5.0	1×10 <sup>-5</sup>
Saliva	1×10 <sup>-10</sup>	10.0	4.0	1×10 <sup>-4</sup>
Milk	1×10 <sup>-11</sup>	11.0	3.0	1×10 <sup>-3</sup>
Human blood, tears	1×10 <sup>-12</sup>	12.0	2.0	1×10 <sup>-2</sup>
Egg white, seawater	1×10 <sup>-13</sup>	13.0	1.0	1×10 <sup>-1</sup>
Baking soda	1×10 <sup>-14</sup>	14.0	0.0	1 (1×10 <sup>-0</sup> )
Borax				
Milk of magnesia				
Lime water				
Household ammonia				
Household bleach				
NaOH, 0.1 M				

Determine the pH of 0.50 M HF solution at 25°C.  $K_a = 7.1 \times 10^{-4}$

1<sup>ST</sup> Write & Balance "Reaction"



2<sup>nd</sup> Write Equilibrium Expression

$$K_a = \frac{[\text{H}^+][\text{F}^-]}{[\text{HF}]}$$

### Initial Change Equilibrium

Determine pH of 0.50 M HF solution  $K_a = 7.1 \times 10^{-4}$

	$\text{HF (aq)} = \text{H}^+ (\text{aq}) + \text{F}^- (\text{aq})$		
Initial (M):	0.50	0.00	0.00
Change (M):	-x	+x	+x
Eqm (M):	0.50 - x	x	x

$$K_a = \frac{[\text{H}^+][\text{F}^-]}{[\text{HF}]}$$

$K_a = 7.1 \times 10^{-4}$ ;  $[\text{HF}] = 0.50 - x$ ;  $[\text{H}^+] = [\text{F}^-] = x$

$$7.1 \times 10^{-4} = \frac{[x][x]}{[0.50 - x]} = \frac{x^2}{0.50 - x} \approx \frac{x^2}{0.50}$$

$$x^2 \cong (7.1 \times 10^{-4})(0.50) \cong 3.55 \times 10^{-4}$$

$$x \cong 1.9 \times 10^{-2}$$

### WAS THE APPROXIMATION VALID ?

$$7.1 \times 10^{-4} = \frac{[x][x]}{[0.50 - x]} = \frac{x^2}{0.50 - x} \approx \frac{x^2}{0.50}$$

No!

Why not ?

Because  $x \cong 1.9 \times 10^{-2}$  is not small compared to 0.50

$$0.50 - x \neq 0.50$$

### VALID APPROXIMATIONS ?

What was the difference between the two examples { HCN(aq) and HF(aq) } ?

Both are monoprotic acids

Both has an initial concentration of 0.50 M

Right the difference was in the size of  $K_a$

$K_a = 7.1 \times 10^{-4}$  for HF

$K_a = 4.9 \times 10^{-10}$  for HCN

What is the pOH of a 0.001M monoprotic weak acid whose  $K_a$  is  $1.6 \times 10^{-10}$ ?

	$\text{HA (aq)} = \text{H}^+ (\text{aq}) + \text{A}^- (\text{aq})$		
Initial	0.001	0.00	0.00
Change	-x	+x	+x
Equil	0.001 - x	x	x

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} = \frac{(x)(x)}{(0.001)} = 1.6 \times 10^{-10}$$

$$\text{pH} = -\log [\text{H}^+] = -\log x = -\log (4.0 \times 10^{-7}) = 6.4$$

$$\text{pH} + \text{pOH} = 14 \quad \text{pOH} = 7.6$$



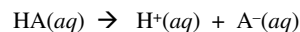
% dissociation of a 0.001M monoprotic weak acid whose  $K_a$  is  $1.6 \times 10^{-10}$  ?

$$\% \text{ Dissociation} = \frac{[\text{H}^+]}{[\text{HA}]} \times 100\%$$

$$\% \text{ Dissociation} = \frac{[4.0 \times 10^{-7}]}{[1 \times 10^{-3}]} \times 100$$

$$\% = 4 \times 10^{-2}$$

What is the pH of a 0.001M monoprotic strong acid ?



Initial      0.001      0.00      0.00

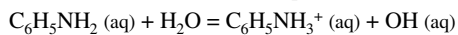
Change    - 0.001    +0.001    +0.001

End        0.000      0.001      0.001

$$\text{pH} = -\log [\text{H}^+] = -\log 0.001 = 3$$

Find pOH of a 0.10 M solution of Aniline ( $\text{C}_6\text{H}_5\text{NH}_2$ ),  $K_b = 3.8 \times 10^{-10}$

Write, Balance and interpret

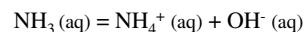


I	0.10	0	0
C	- x	x	x
E	0.10	x	x

$$K_b = \frac{[\text{C}_6\text{H}_5\text{NH}_3^+][\text{OH}^-]}{[\text{C}_6\text{H}_5\text{NH}_2]} = \frac{[x][x]}{[0.10 - x]} = 3.8 \times 10^{-10}$$

$$x = [\text{OH}^-] = 6.2 \times 10^{-5} \quad \text{pOH} = -\log[\text{OH}^-] = 4.2$$

pH of a 0.10 M solution of ammonia,  $K_b = 1.8 \times 10^{-5}$



$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]}$$

$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = \frac{[x][x]}{[0.10 - x]} = 1.8 \times 10^{-5}$$

$$[\text{OH}^-] = 1.34 \times 10^{-3}$$

$$\text{pOH} = -\log [\text{OH}^-] = 2.9$$

$$\text{pH} = 14 - 2.9 = 11.1$$

#### Acid-Base Properties of Salts

- Salts that produce neutral solutions are those formed from strong acids and strong bases. *For example NaCl*
- Salts that produce basic solutions are those formed from weak acids and strong bases. *For example MgCl<sub>2</sub>*
- Salts that produce acidic solutions are those formed from strong acids and weak bases. *For example NaClO*