

# CORROSION AND ITS PREVENTION

# Objective

- What is corrosion
- Classification of corrosion
- Mechanism of corrosion
- Types of corrosion
- Corrosion prevention methods

# Introduction

- Corrosion is defined as unintentional destruction of a solid body by chemical or electrochemical reactions starting from the surface.
- Non-Metals corrode by chemical reactions & metals mostly by electrochemical reactions.
- Metals are at high energy levels & hence there is natural tendency to go to the low energy state i.e. they try to form oxides, hydroxides, carbonates, sulphides etc. depending on the type of environment to which they are exposed.

# Chemical vs. Electrochemical Reactions

- Chemical reactions are those in which elements are added or removed from a chemical species
- Electrochemical reactions are chemical reactions in which not only elements may be added or removed from a chemical species but at least one of the species undergoes a change in the number of valance electron
- Corrosion processes are electrochemical in nature

# Classification of corrosion

- Dry corrosion
- Wet corrosion

# Dry corrosion

- Dry corrosion occurs when the metals are exposed to gaseous environment
- The extent of corrosion & protective values depends on the following factors
  1. Chemical affinity between the environment & the metal.
  2. Protective value of film.
  3. Nature of film formed.
  4. Adhesion between the film & the metal surface.
  5. For non ferrous film, the extent of corrosion depends on the electronic & ionic conductivities of the film.

# Pilling & Bedworth Rule

- This rule gives the idea about the nature of the film formed i.e. whether the film is porous or nonporous.

Volume of oxide

- Pilling & Bedworth Ratio =  $\frac{\text{Volume of oxide}}{\text{Volume of equivalent amount of metal consumed during oxidation}}$

$$= M_d/m_D$$

# Formation & Growth Of Film

- The formation & growth of films occur by three successive stages
  1. Adsorption
  2. Chemisorptions
  3. Growth of film
    - 3.1 Growth of non porous film
    - 3.2 Growth of porous film



# Wet corrosion

- Wet corrosion occur when a metal or an alloy comes in contact with an aqueous solution of salt, acid or alkali by an electrochemical type of reaction.
- When a metal is immersed in an aqueous electrolyte, it dissolve / dissociate into metal ion + electron.
- This tendency of metal is called as electrolytic pressure or solution pressure ( $p$ )
- The dissolved ion from the solution tend to deposit on the immersed metal surface & oppose the solution pressure of metal. This tendency is called as osmotic pressure of metal ion ( $p$ )
- When these forces become equal, equilibrium is reached and under this condition, a definite number of electrons accumulate on the metal surface & a definite potential will be developed on the metal piece.

**TABLE 12.1 Standard Electrode Potentials at 25°C\***

	<b>Oxidation (corrosion) reaction</b>	<b>Electrode potential, <math>E^\circ</math> (volts vs. standard hydrogen electrode)</b>
<p><b>More cathodic</b> <b>(less tendency to corrode)</b></p> <p>↑</p>	$\text{Au} \rightarrow \text{Au}^{3+} + 3e^-$	+1.498
	$2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4e^-$	+1.229
	$\text{Pt} \rightarrow \text{Pt}^{2+} + 2e^-$	+1.200
	$\text{Ag} \rightarrow \text{Ag}^+ + e^-$	+0.799
	$2\text{Hg} \rightarrow \text{Hg}_2^{2+} + 2e^-$	+0.788
	$\text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + e^-$	+0.771
	$4(\text{OH})^- \rightarrow \text{O}_2 + 2\text{H}_2\text{O} + 4e^-$	+0.401
	$\text{Cu} \rightarrow \text{Cu}^{2+} + 2e^-$	+0.337
	$\text{Sn}^{2+} \rightarrow \text{Sn}^{4+} + 2e^-$	+0.150
	$\text{H}_2 \rightarrow 2\text{H}^+ + 2e^-$	0.000
<p><b>More anodic</b> <b>(greater tendency to corrode)</b></p> <p>↓</p>	$\text{Pb} \rightarrow \text{Pb}^{2+} + 2e^-$	-0.126
	$\text{Sn} \rightarrow \text{Sn}^{2+} + 2e^-$	-0.136
	$\text{Ni} \rightarrow \text{Ni}^{2+} + 2e^-$	-0.250
	$\text{Co} \rightarrow \text{Co}^{2+} + 2e^-$	-0.277
	$\text{Cd} \rightarrow \text{Cd}^{2+} + 2e^-$	-0.403
	$\text{Fe} \rightarrow \text{Fe}^{2+} + 2e^-$	-0.440
	$\text{Cr} \rightarrow \text{Cr}^{3+} + 3e^-$	-0.744
	$\text{Zn} \rightarrow \text{Zn}^{2+} + 2e^-$	-0.763
	$\text{Al} \rightarrow \text{Al}^{3+} + 3e^-$	-1.662
	$\text{Mg} \rightarrow \text{Mg}^{2+} + 2e^-$	-2.363
	$\text{Na} \rightarrow \text{Na}^+ + e^-$	-2.714

\* Reactions are written as anodic half-cells. The more negative the half-cell reaction, the more anodic the reaction is and the greater the tendency for corrosion or oxidation to occur.

**Galvanic Scale  
of Metals in Sea Water**

NOTE: Potentials vary with the actual  
composition of the material.

Material	Potential
Magnesium and its Alloys .....	-1.50
Zinc .....	-1.03
Aluminum and its Alloys .....	-0.75
Cast Iron .....	-0.61
Carbon Steel .....	-0.61
Type 430 Stainless (Active) .....	-0.57
Type 304 Stainless (Active) .....	-0.53
Type 410 Stainless (Active) .....	-0.52
Silicon Bronze .....	-0.40
Copper .....	-0.36
Yellow Brass—268 .....	-0.36
Red Brass—230 .....	-0.33
Aluminum Bronze .....	-0.32
Tin Bronze—(G & M) .....	-0.31
Admiralty Brass .....	-0.29
Copper-Nickel	
90-10 .....	-0.28
80-20 .....	-0.27
70-30 .....	-0.25
Nickel—200 .....	-0.20
Silver Solder .....	-0.20
Inconel—600 .....	-0.17
Monel .....	-0.13
Stainless Steel (Passive) .....	-0.10
Silver/Silver Chloride half cell (Reference) .....	0.00
Graphite .....	+0.20

More Active (Less Noble)



More Passive or Noble

What is the voltage difference between Zinc (Zn) and Copper (Cu)?

An. 0.67v

What is more noble than Stainless Steel (Passive)?

An. Graphite

# Mechanism Of Wet Corrosion

- The reaction at anode is always oxidation reaction & is associated with the dissolution of metal i.e.

Metal  $\longrightarrow$  Metal ions + electron

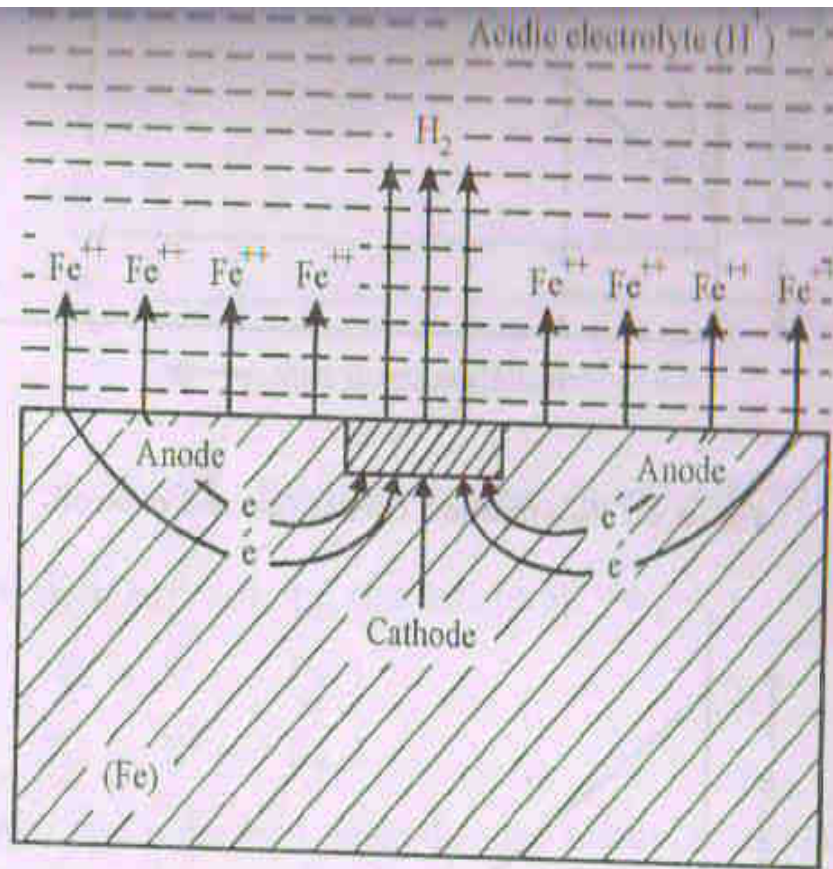
- The reaction at cathode is always a reduction reaction with no corrosion of cathode & varies depending on the nature of electrolyte in contact

1. Hydrogen evolution :
2. Oxygen absorption :

# 1. Hydrogen evolution :

- The hydrogen evolution occurs at the cathode in concentrated acidic environment ( $\text{pH} < 4$ ) usually iron surface is covered with oxide at least at few points or it may difference in hydrogen over potential from point to point
- Due to this some areas act as cathode with respect to other areas which behaves as anode of the cell & galvanic corrosion occurs.
- At the anode :  $\text{Fe} \rightarrow \text{Fe}^{++} + 2\text{e}$
- At the cathode :  $2\text{H}^+ + 2\text{e} \rightarrow \text{H}_2$
- it is clear from the reaction that hydrogen evolution type of corrosion occurs by simple displacement of hydrogen ion from acidic solution by metal ion.

continue .....



**Fig. 6.10 : Hydrogen evolution mechanism of corrosion.**

At the anode :



## 2. Oxygen Absorption

- Oxygen absorption mechanism of corrosion occurs in mild acidic or alkaline environment ( $\text{pH} > 4$ )
- The above process for the rusting of iron taking an electrolyte of aqueous solution of sodium chloride.
- The area which are not covered with the oxide become anodic with respect to the areas covered with the oxide which become cathodic & corrosion occurs by the following reactions :
- Reaction at anode :  $\text{Fe} \rightarrow \text{Fe}^{++} + 2\text{e}$  &  $\text{Fe}^{++} + 2\text{Cl}^- \rightarrow \text{FeCl}_2$
- Reaction at cathode :  $4\text{e} + \text{O}_2 + 2\text{H}_2\text{O} \rightarrow 4\text{OH}^-$
- $\text{OH}^- + \text{Na}^+ \rightarrow \text{NaOH}$
- Both the anodic product  $\text{FeCl}_2$  & cathodic product  $\text{NaOH}$  are soluble in water & diffuse towards each other.

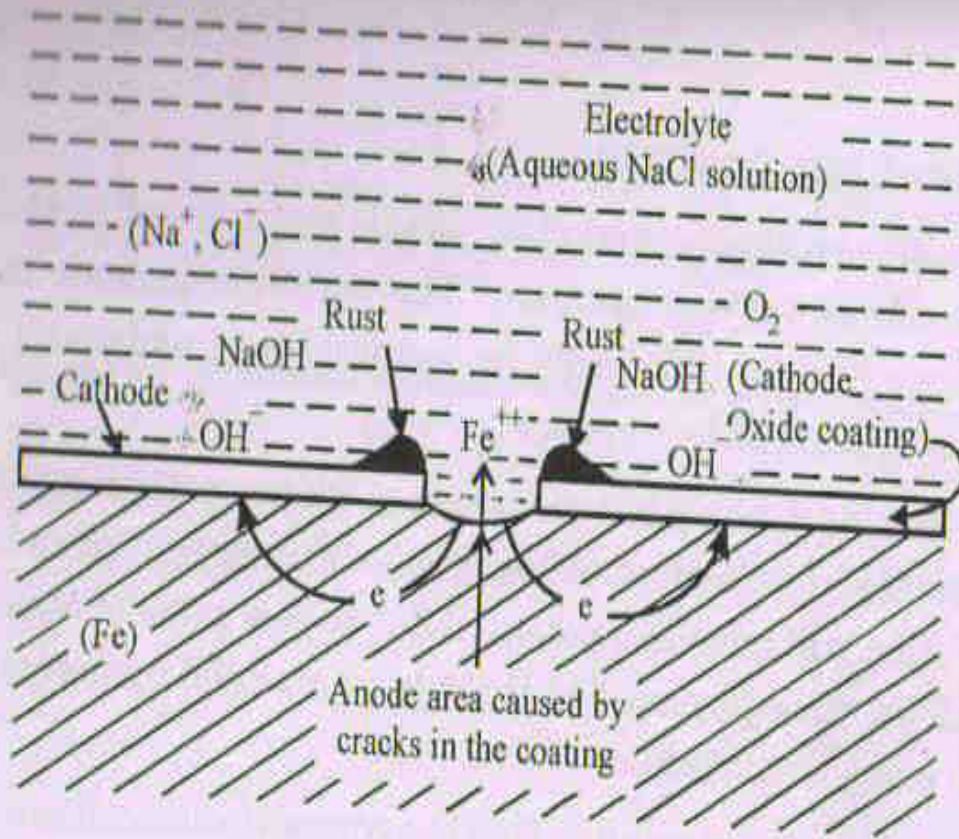
continue....

- When both meet ferrous hydroxide is formed. In the presence sufficient dissolved oxygen, ferrous hydroxide is further oxidized to ferric hydroxide which has very little solubility in water & precipitate out as yellow rust.
- It is clear that there is no concentration polarization at both the electrode.



of sodium chloride.

of iron taking an electrolyte of aqueous



**Fig. 6.11 : Oxygen absorption mechanism of corrosion.**

areas which are not covered with the oxide become anodic with respect to the areas which are covered with the oxide.

# Types Of Corrosion

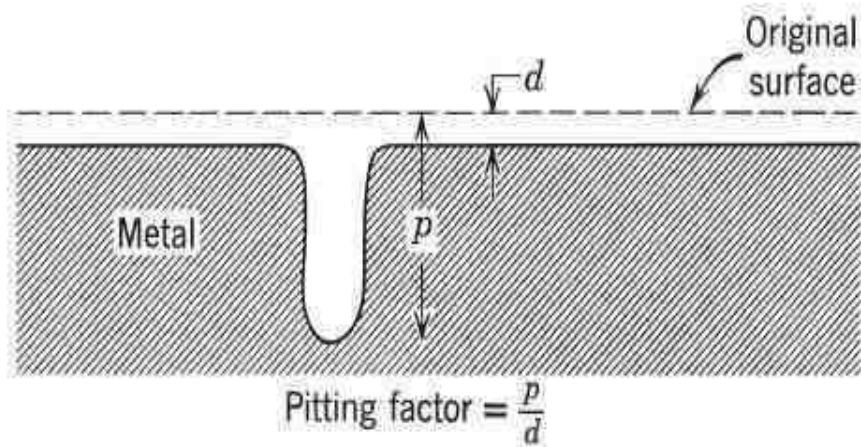
- General corrosion
- Pitting corrosion
- Crevice corrosion
- Intergranular corrosion
- Stress corrosion cracking
- Erosion – corrosion
- Cavitation corrosion
- Corrosion fatigue
- Hydrogen blistering
- High temperature corrosion

- General / Uniform Corrosion



- Corrosion proceeds at the same rate throughout the area exposed to the environment & there is no clearly defined anode & cathode areas.
- the extent of corrosion can be expressed by loss in weight per unit area or by average penetration depth

# Pitting Corrosion



- Pitting corrosion is a localized accelerated corrosion resulting in the formation of cavities around which the metal is relatively unattacked.

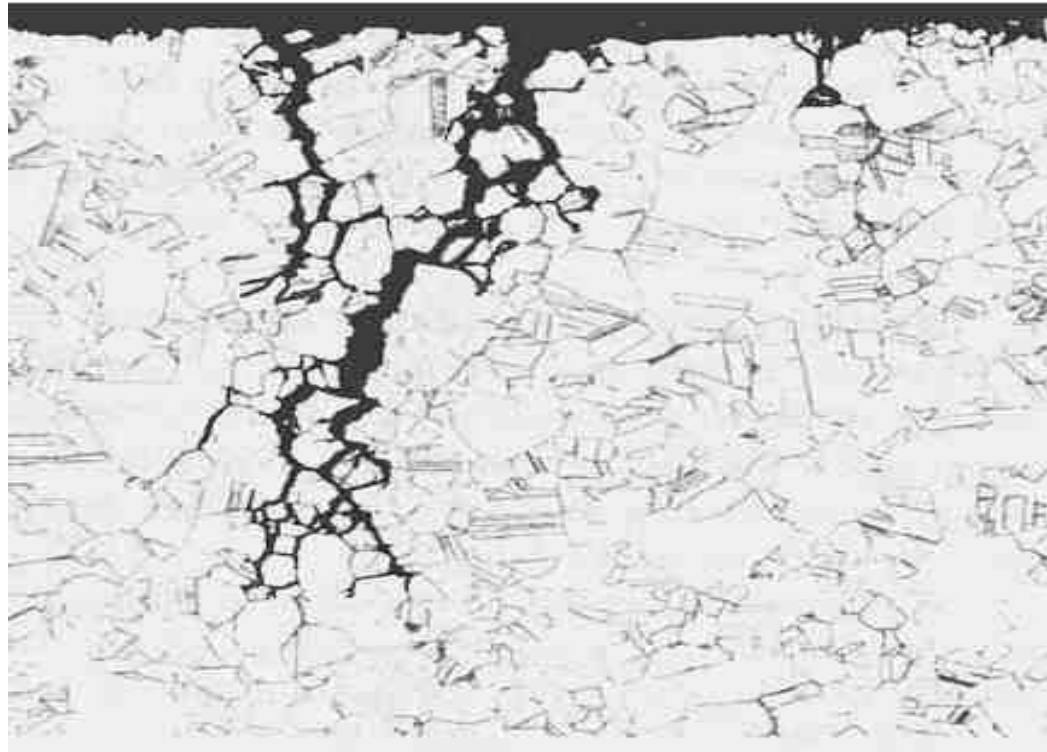
- Small anodic area & large cathodic areas results in high anodic current density leading to rapid corrosion of small anodic areas forming pit or pinholes
  - This results in rapid perforation of metal sharply reducing the mechanical properties of of the component.
  - Pitting has more effect on fatigue strength
  - Pitting corrosion can occur under following situations:
    1. Due to break in the protective coating
    2. Due to destruction of passive layer at few points under certain environmental conditions.
    3. Differential aeration corrosion may lead to pitting corrosion
- continue...

- Crevice corrosion, corrosion take place in crevices bcz solutions retained at this place and takes longer time to dry out. When this occurs, the severity of attack is more severe at crevices. Crevices are formed bcz of the metal contact with another piece of the same or other metal or with a nonmetallic material. Corrosion in crevice is due to deficiency of O<sub>2</sub>, Acidity changes,

- Crevice Corrosion

- narrow crevice filled with ionized solution
- Oxygen-rich on the outside, oxygen-poor on the inside
- metals oxidize with salt anions  $\text{FeCl}_2$  and pH rises in cathodic zone
- $\text{H}^+$  may destroy passivity

# Intergranular Corrosion

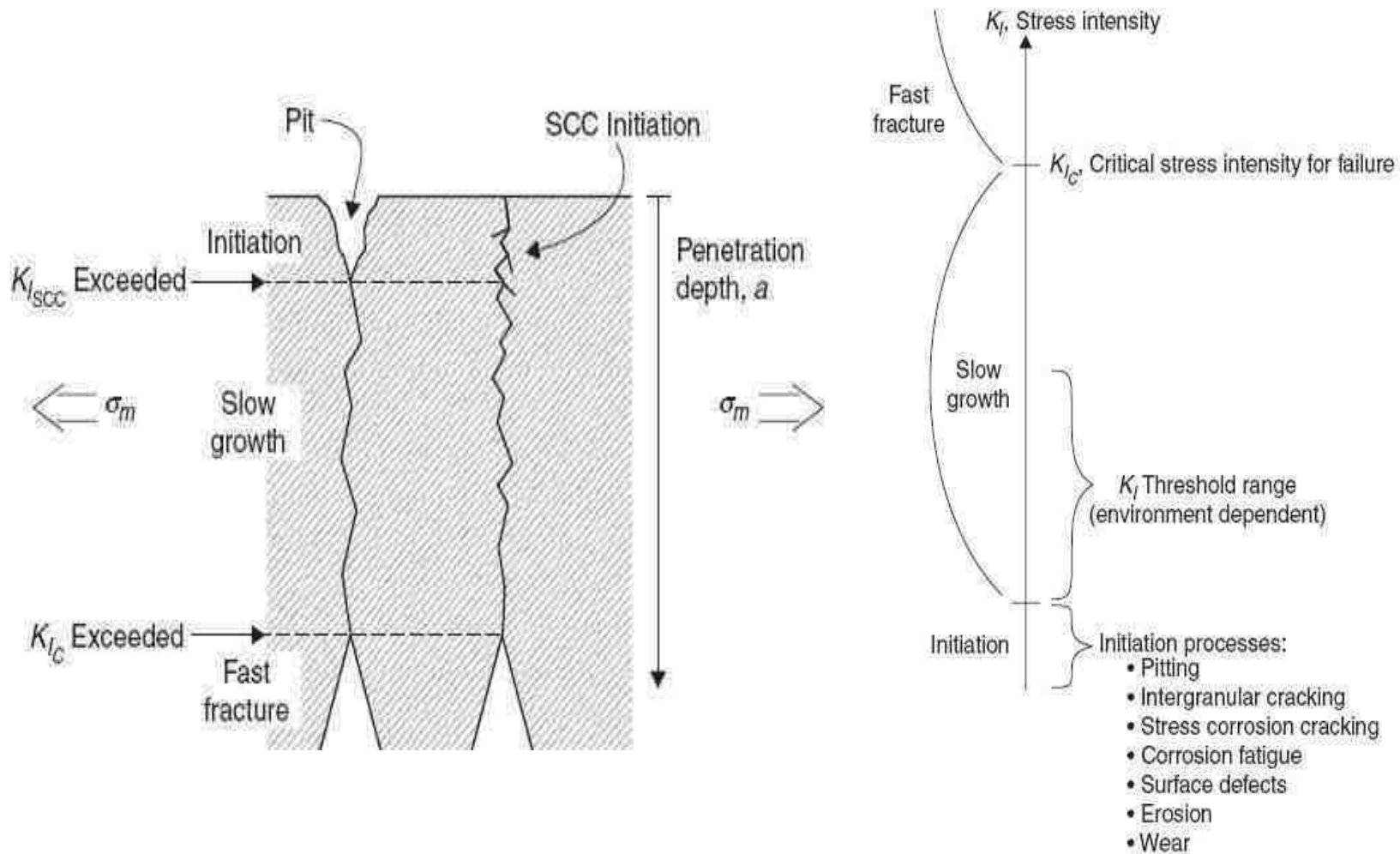


- This types of corrosion occurs at the grain boundaries or at the region adjacent to the grain boundaries due to precipitation of some phase at the grain boundaries



- The precipitate phase makes the material sensitive to corrosion
- The grain boundary phase or the region adjacent to grain boundary become anodic & get preferentially corroded
- This type of corrosion can occur even without the precipitation of phase at the grain boundaries, this is because the grain boundary regions being high energy region will get preferentially corroded due to their low electrode potential compared to the electrode potential of grain
- E.g. Corrosion of Austenitic stainless steels due to precipitation of complex chromium carbide along grain boundaries.
- Weld decay.

# Stress corrosion cracking



- This type of corrosion occurs due to presence of stresses in the material
- The stresses area become anodic with respect to the other areas & get corroded by forming stress cell.
- It has been observed that if the stresses are tensile, it leads to cracking of the material in due course of time when exposed to certain environmental conditions & hence the phenomenon is known as SCC.
- The static tensile stress present in the material may be residual (internal) or applied (external).
- Internal stresses are developed due to cold working processes, or due to rapid cooling, poor design, precipitation of second phase.
- External stresses are produced due to application of external load on the components.

- Erosion – corrosion type of corrosion occurs by the simultaneous effect of corrosion & erosion produced by the turbulent flow of electrolyte, & also by the rubbing action of solid particle over a metal surface.
- This type of corrosion can occur in any metal & alloy.
- In many cases, it has been observed that the damage to the metal is due to the breaking of protective coating of corrosion product & coating is not get repaired due to turbulence flow of electrolyte.
- This type of corrosion is usually occurs in the regions where the flow of electrolyte is disturbed e.g. bend in pipes, condenser tube, valve seat in in water fitting etc.

# Corrosion prevention Methods

## Inhibitors

- Inhibitors is a substance which effectively decreases the corrosion rate of a metal when added in small amount to the corrosive environment.
  - These substances control the anodic or cathodic reactions reducing the corrosion of metals.
1. Anodic Inhibitors
  2. Cathodic Inhibitors

# Anodic Inhibitors

- Anodic inhibitors when added to the electrolyte combine with the newly formed metal ions at the anode & form a precipitate.
- This precipitate deposits on the anode surface forming a protective layer which stops or reduces the corrosion.
- Thus the local anode areas get polarized i.e. an increase in potential occurs at these areas.
- Anodic inhibitors work effectively when they are added in sufficient amount.

# Cathodic Inhibitors

- Cathodic inhibitors reduce the corrosion by stopping the cathodic reaction
- **In acidic electrolyte**, cathodic reactions is of hydrogen evolution type
- In such case, corrosion can be reduced by reducing the diffusion of hydrogen ion to the cathode or by increasing the over potential of hydrogen.
- The diffusion of hydrogen ion is reduced by using certain organic compounds.
- hydrogen over potential is increased by adding salts of As, Sb & Bi.

# Protective Coatings / Wrapping

- Provide barrier between metal and environment.
- Coatings may act as sacrificial anode or release substance that inhibit corrosive attack on substrate.
- Metal coatings :
  - **Noble – silver, copper, nickel, Cr, Sn, Pb on steel. Should be free of pores/discontinuity coz creates small anode-large cathode leading to rapid attack at the damaged areas.**
  - **Sacrificial – Zn, Al, Cd on steel. Exposed substrate will be cathodic & will be protected.**
  - **Application – hot dipping, flame spraying, cladding, electroplating, vapor deposition, etc.**



- Surface modification – to structure or composition by use of directed energy or particle beams. E.g ion implantation and laser processing.
- Inorganic coating : cement coatings, glass coatings, ceramic coatings, chemical conversion coatings.
- Chemical conversion – anodizing, phosphatizing, oxide coating, chromate.
- Organic coating : paints, lacquers, varnishes. Coating liquid generally consists of solvent, resin and pigment. The resin provides chemical and corrosion resistance, and pigments may also have corrosion inhibition functions.

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- Paints, pigments are also widely used for the protection of metallic component.

### 3. Anodized Coating (Chemical Conversion Coating)

- In atmospheric conditions Al, Al alloys, Ti, Ti alloys form a thin film of oxide on their surfaces.
- This thin film of oxide provides a good resistance to further corrosion of the above materials.
- However, under the normal atmosphere conditions the thickness of oxide layer is very small & does not protect the metal from corrosion under severe condition of exposure.
- to make this materials highly corrosion resistant, the naturally existing film of oxide is increased in thickness by electrolysis.

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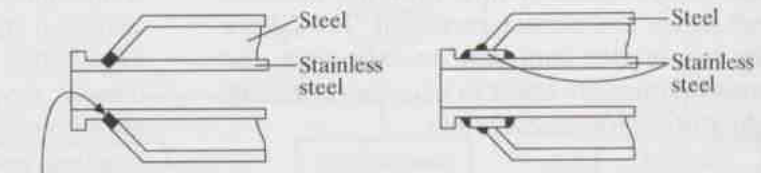
- The electrolysis process used for increasing thickness of oxide film is called anodizing.
- The metal is not coated by any other material as is done in the previous method, but the surface of metal is converted into oxide & hence they can be called as chemical conversion coating.

# Anodic Protection (Cathodic coating)

- Here the metal get protect anodic by the application of coating of cathodic material.
- Coating of Ni & Cr on Fe & steel, Coating of Au, Ag on brasses or bronzes.
- When the coating is dense, non porous & continuous, the electrolyte does not come in contact with the component & hence the component does not corrode.

# Cathodic protection (Anodic Coating)

- Here the metal get protect cathode by the application of coating of anodic material.
- Coating of Zn & Cd on iron & steel
- When the coating is dense, nonporous & continuous, the electrolyte does not come in contact with the component & hence the component does not corrode.
- The coating metal completely separate the electrolyte from metal.
- Such coating completely prevent the component from corrosion even in the presence of discontinuous or breaks.

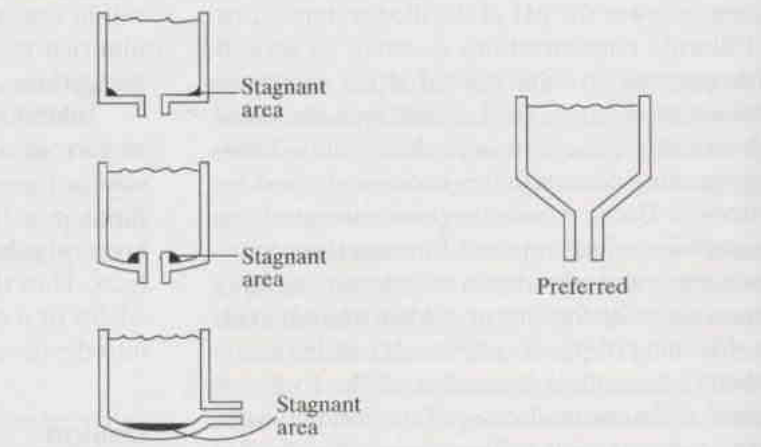


Possible dilution  
(steel can mix with stainless)

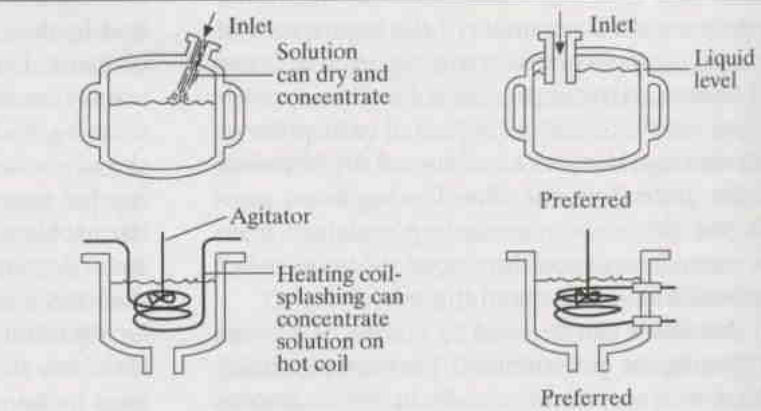
(a) Prevent base metal dilution



(b) Crevice control



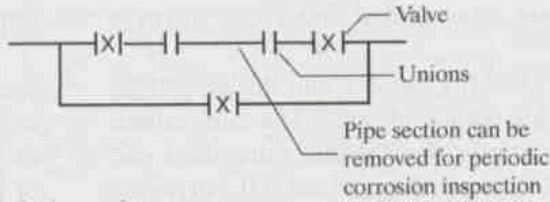
(c) Provide proper drainage



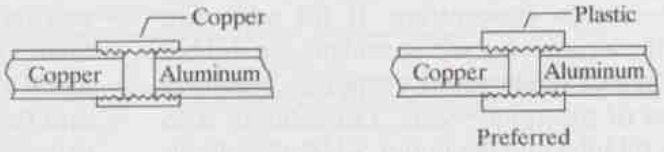
(d) Prevent solutions from drying and concentrating

# DESIGN for Corrosion

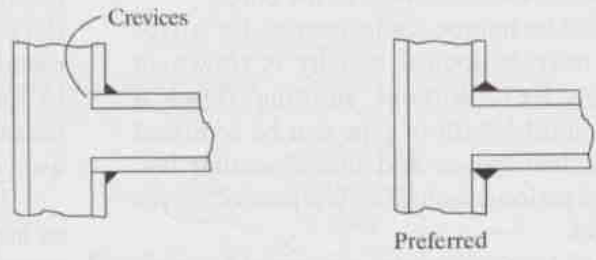




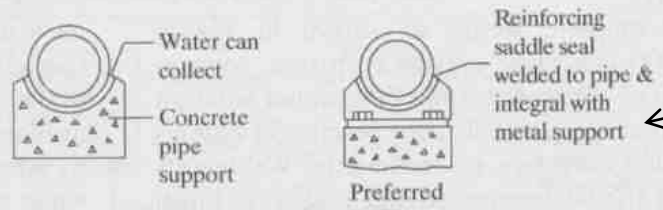
(e) Provide for inspection



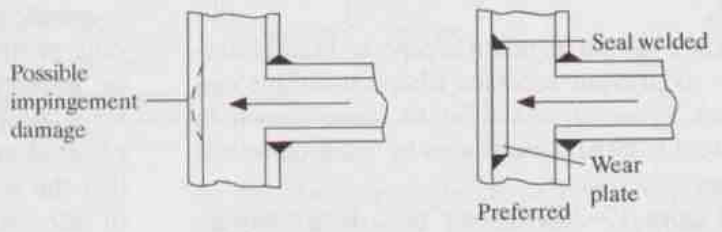
(f) Prevent galvanic couples



(g) Avoid incomplete weld penetration



(h) Avoid water accumulation in outdoor construction



(i) Use wear plates to minimize corrosive wear

## DESIGN for Corrosion

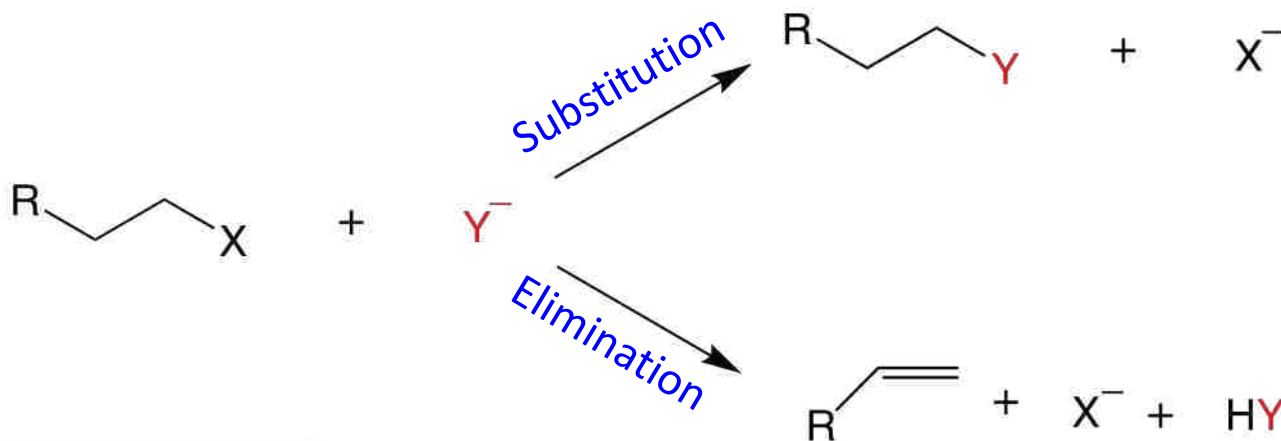
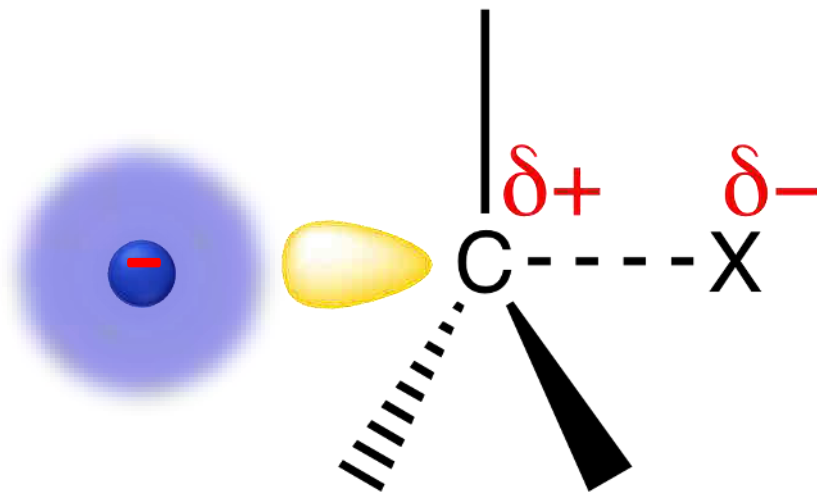
Bracket easier to replace than pipe!

- Avoid sharp corners – paint tends to be thinner at sharp corners and often starts to fail.
- Provide for easy drainage (esp tanks) – avoid remaining liquids collect at bottom. E.g steel is resistant against concentrated sulfuric acid. But if remaining liquid is exposed to air, acid tend to absorb moisture, resulting in dilution and rapid attack occurs.
- Avoid hot spots during heat transfer operations – localized heating and high corrosion rates. Hot spots also tend to produce stresses – SCC failures.
- Design to exclude air – except for active-passive metals and alloys coz they require O<sub>2</sub> for protective films.
- Most general rule : AVOID HETEROGENEITY!!!

# Substitution and Elimination

Reaction of Alkyl Halides

Organic compounds with an electronegative atom or an electron-withdrawing group bonded to a  $sp^3$  carbon undergo substitution or elimination reactions



Halide ions are good leaving groups. Substitution reactions on these compounds are easy and are used to get a wide variety of compounds

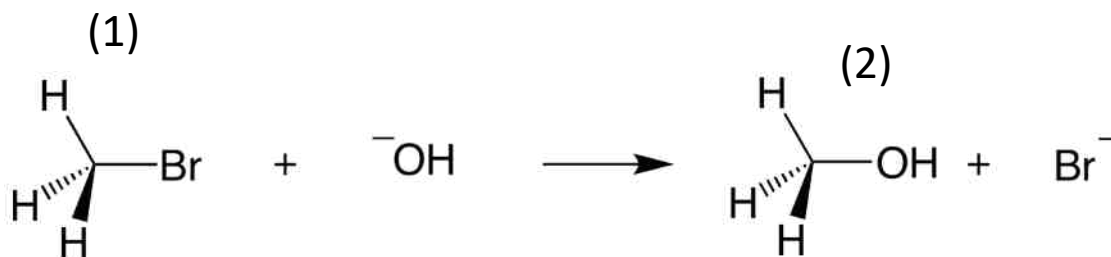
R—F  
alkyl fluoride

R—Cl  
alkyl chloride

R—Br  
alkyl bromide

R—I  
alkyl iodide

# Substitution Reaction with Halides



bromomethane

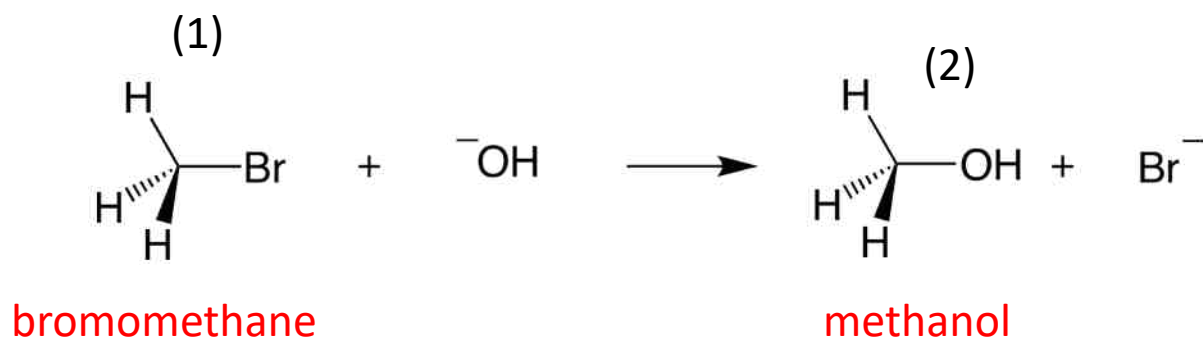
methanol

If concentration of (1) is doubled, the rate of the reaction is doubled.

If concentration of (2) is doubled, the rate of the reaction is doubled.

If concentration of (1) and (2) is doubled, the rate of the reaction quadruples.

# Substitution Reaction with Halides



Rate law:

$$\text{rate} = k [\text{bromoethane}][\text{OH}^-]$$

this reaction is an example of a SN2 reaction.

**S** stands for **substitution**

**N** stands for **nucleophilic**

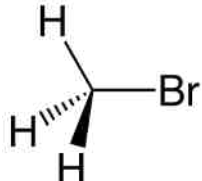
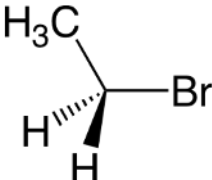
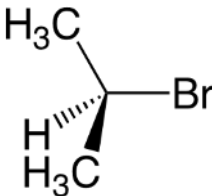
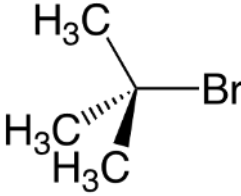
**2** stands for **bimolecular**

# Mechanism of SN2 Reactions

The rate of reaction depends on the concentrations of both reactants.

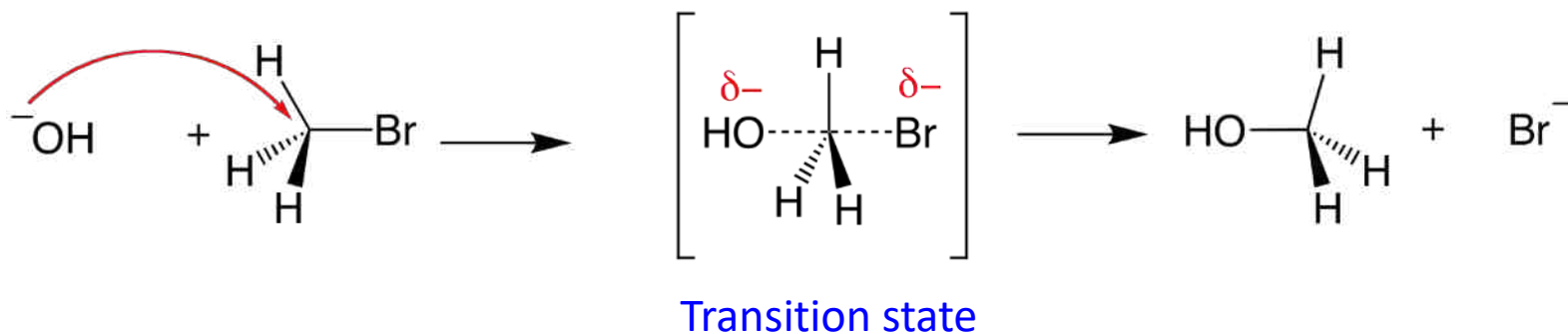
When the hydrogens of bromomethane are replaced with methyl groups the reaction rate slow down.

The reaction of an alkyl halide in which the halogen is bonded to an asymmetric center leads to the formation of only one stereoisomer

Alkyl halide	Relative rate
	1200
	40
	1
	≈ 0

# Mechanism of SN2 Reactions

Hughes and Ingold proposed the following mechanism:

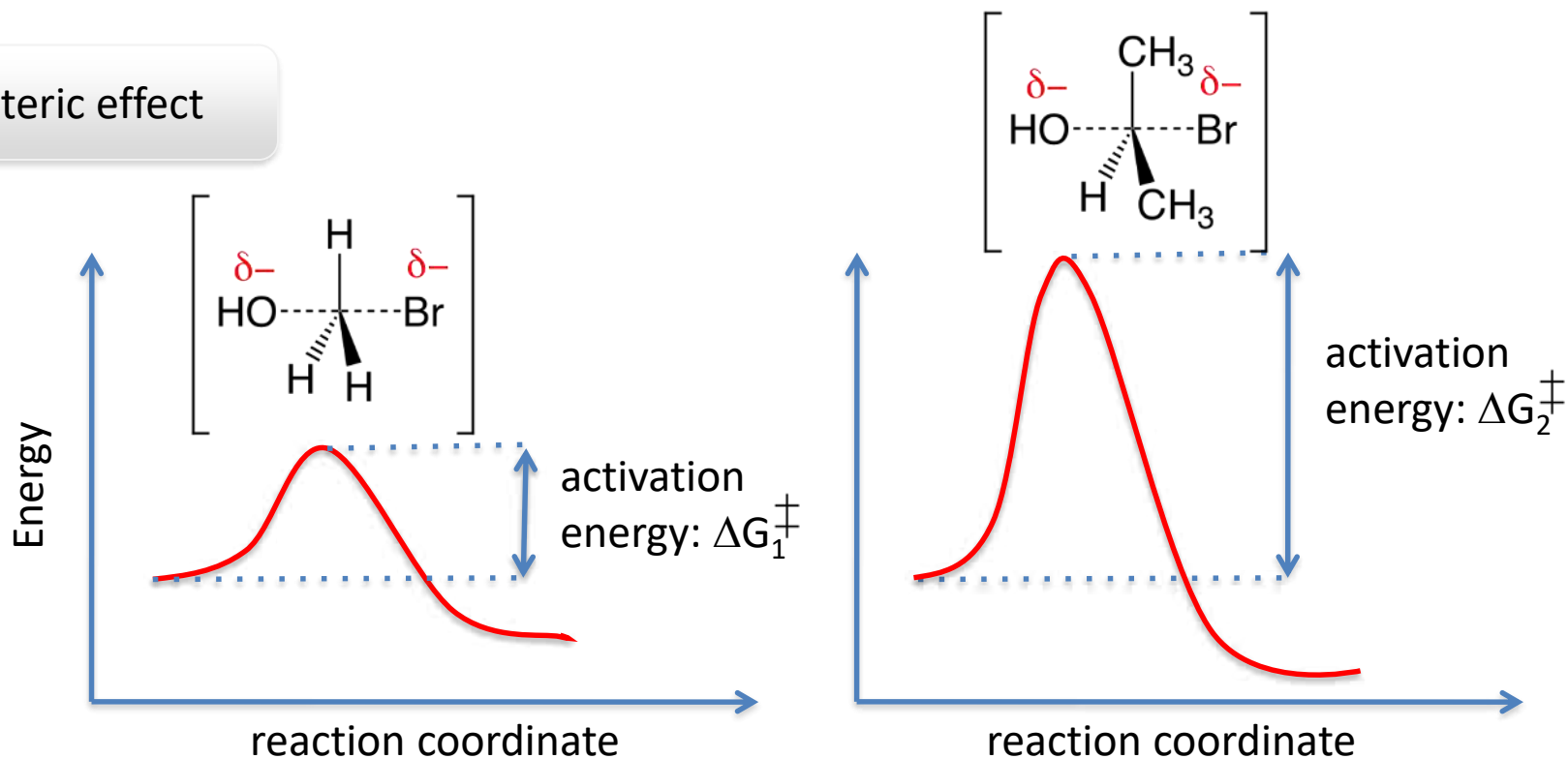


Increasing the concentration of either of the reactant makes their collision more probable.

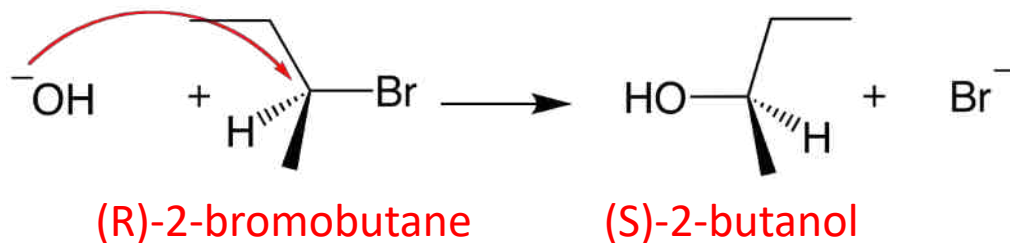


# Mechanism of SN2 Reactions

Steric effect



Inversion of configuration



# Factor Affecting SN2 Reactions

## The leaving group

	<u>relative rates of reaction</u>	<u>pK<sub>a</sub> HX</u>
$\text{HO}^- + \text{RCH}_2\text{I} \longrightarrow \text{RCH}_2\text{OH} + \text{I}^-$	30 000	-10
$\text{HO}^- + \text{RCH}_2\text{Br} \longrightarrow \text{RCH}_2\text{OH} + \text{Br}^-$	10 000	-9
$\text{HO}^- + \text{RCH}_2\text{Cl} \longrightarrow \text{RCH}_2\text{OH} + \text{Cl}^-$	200	-7
$\text{HO}^- + \text{RCH}_2\text{F} \longrightarrow \text{RCH}_2\text{OH} + \text{F}^-$	1	3.2

## The nucleophile

In general, for halogen substitution the strongest the base the better the nucleophile.

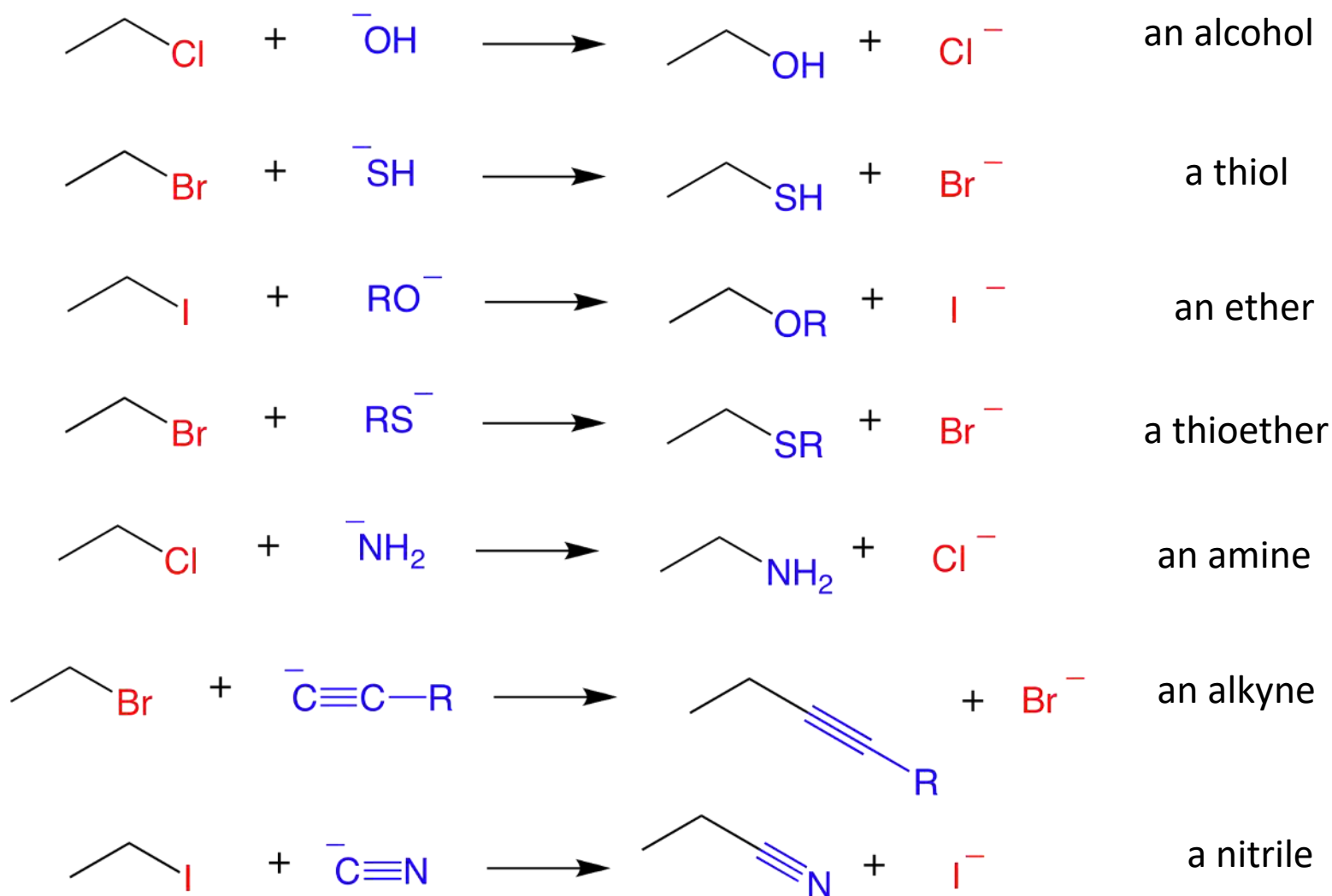


pKa

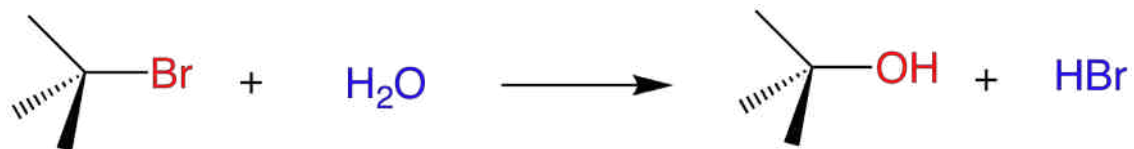


Nucleophilicity

# SN2 Reactions With Alkyl Halides



# Substitution Reactions With Halides



1-bromo-1,1-dimethylethane

1,1-dimethylethanol

If concentration of (1) is doubled, the rate of the reaction is doubled.

If concentration of (2) is doubled, the rate of the reaction **is not** doubled.

Rate law:

$$\text{rate} = k [\text{1-bromo-1,1-dimethylethane}]$$

this reaction is an example of a **SN1** reaction.

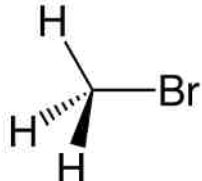
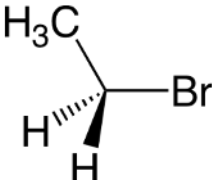
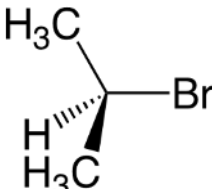
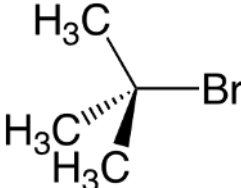
**S** stands for **substitution**  
**N** stands for **nucleophilic**  
**1** stands for **unimolecular**

# Mechanism of SN1 Reactions

The rate of reaction depends on the concentrations of the alkyl halide only.

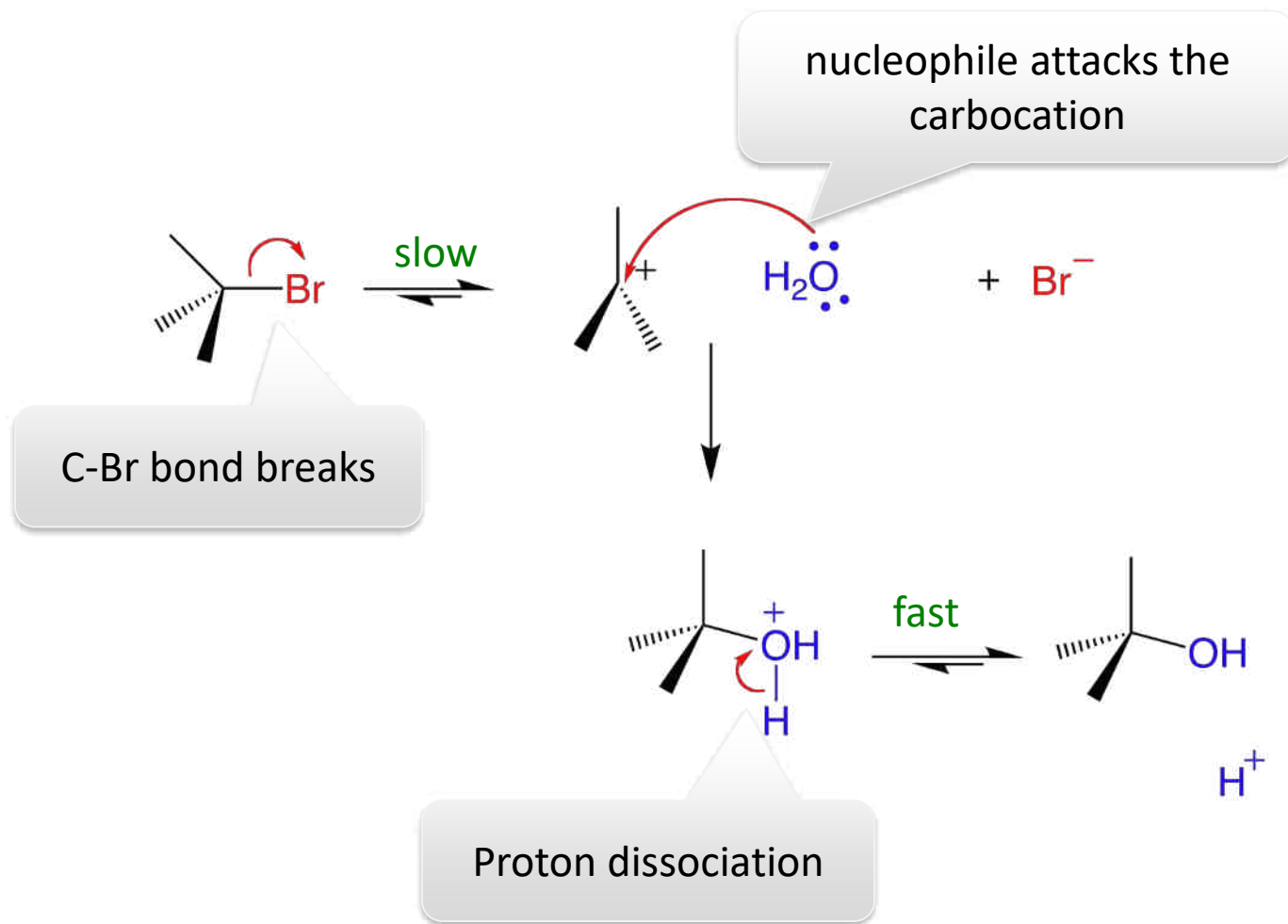
When the methyl groups of 1-bromo-1,1-dimethylethane are replaced with hydrogens the reaction rate slows down.

The reaction of an alkyl halide in which the halogen is bonded to an asymmetric center leads to the formation of two stereoisomers

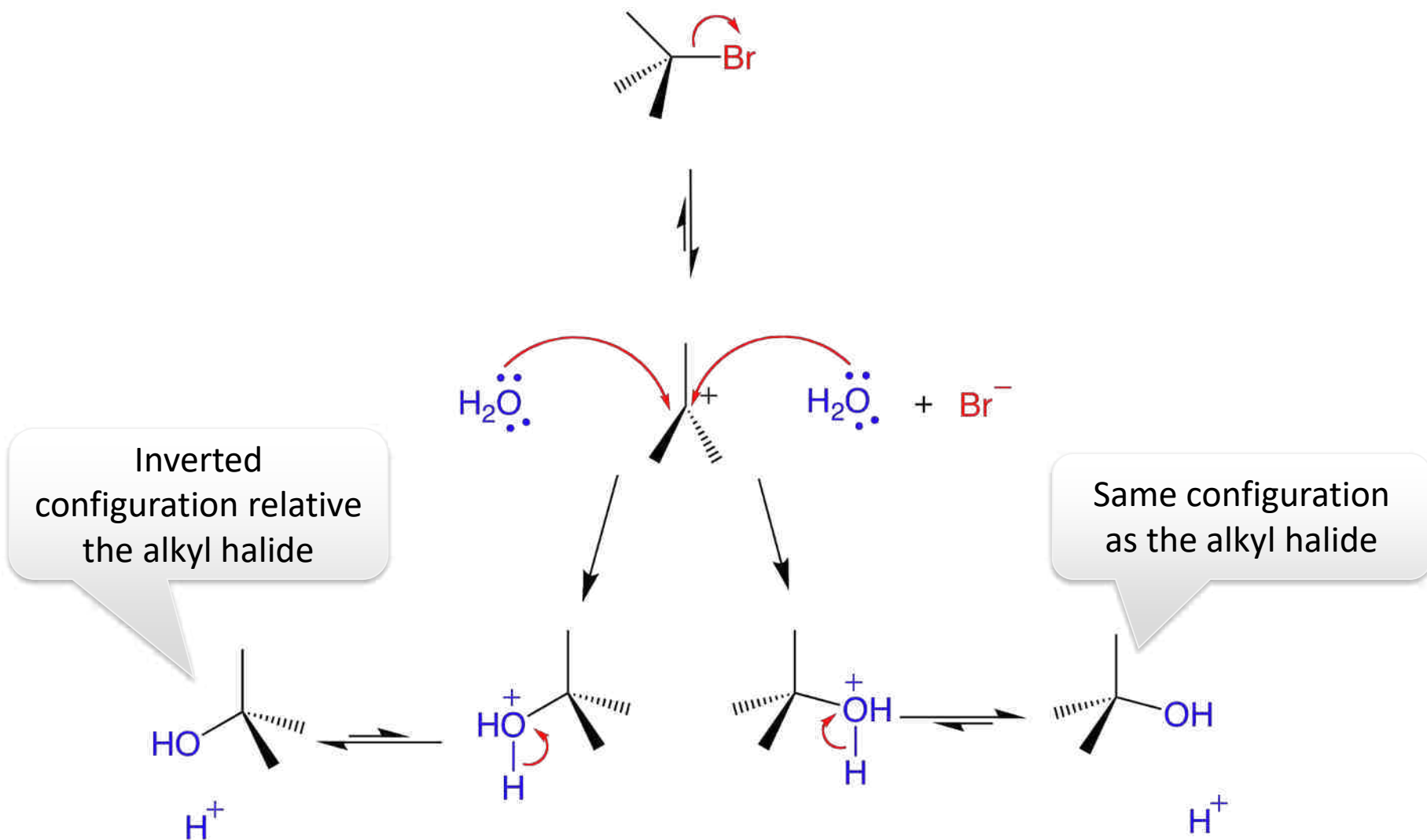
Alkyl halide	Relative rate
	$\approx 0^*$
	$\approx 0^*$
	12
	1 200 000

\* a small rate is actually observed as a result of a SN2

# Mechanism of SN1 Reactions



# Mechanism of SN1 Reactions



# Factor Affecting SN1 reaction

Two factors affect the rate of a SN1 reaction:

- The ease with which the leaving group dissociate from the carbon
- The stability of the carbocation

The more the substituted the carbocation is, the more stable it is and therefore the easier it is to form.

As in the case of SN2, the weaker base is the leaving group, the less tightly it is bonded to the carbon and the easier it is to break the bond

The reactivity of the nucleophile has no effect on the rate of a SN1 reaction



# Comparison SN1 – SN2

SN1	SN2
A two-step mechanism	A one-step mechanism
A unimolecular rate-determining step	A bimolecular rate-determining step
Products have both retained and inverted configuration relative to the reactant	Product has inverted configuration relative to the reactant
Reactivity order: $3^\circ > 2^\circ > 1^\circ > \text{methyl}$	Reactivity order: $\text{methyl} > 1^\circ > 2^\circ > 3^\circ$

# Elimination Reactions



1-bromo-1,1-dimethylethane

2-methylpropene

Rate law:

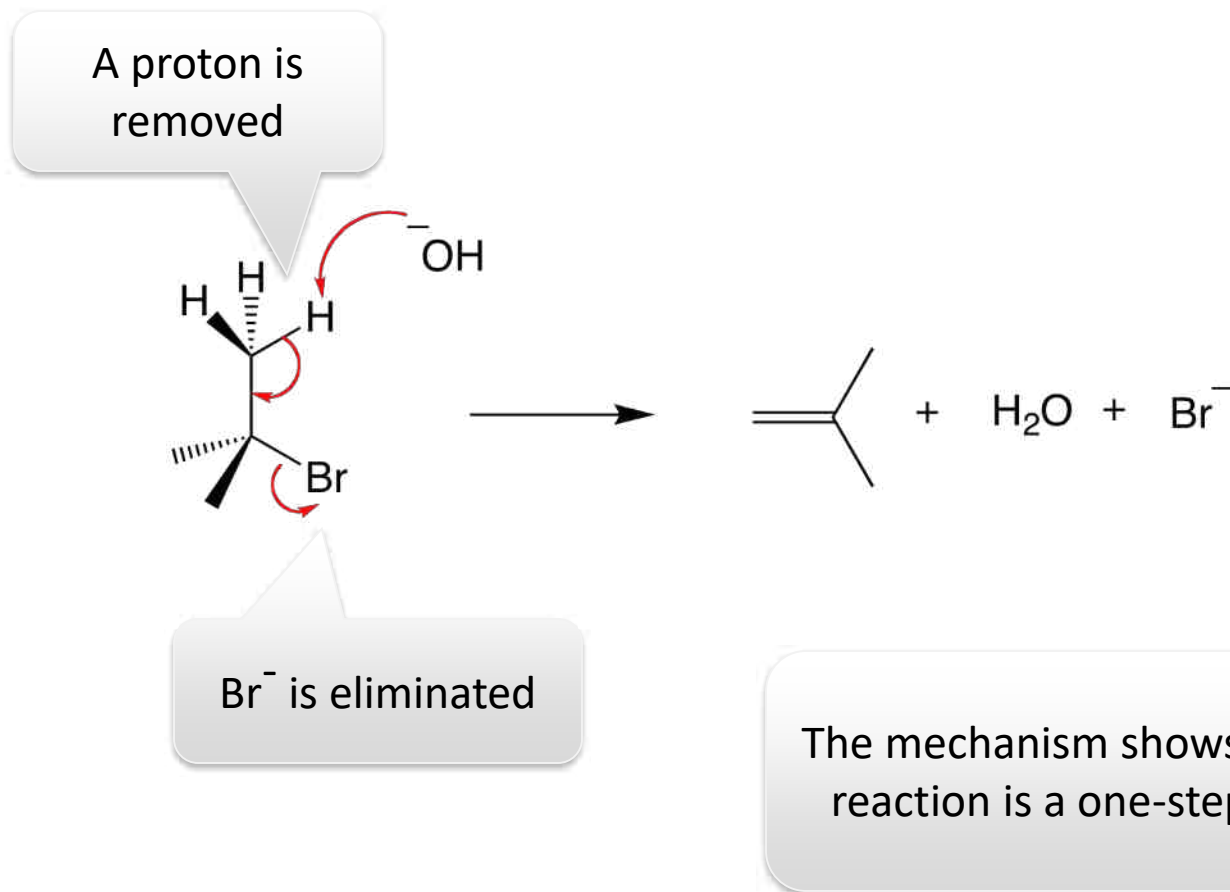
$$\text{rate} = k [\text{1-bromo-1,1-dimethylethane}][\text{OH}^-]$$

this reaction is an example of a E2 reaction.

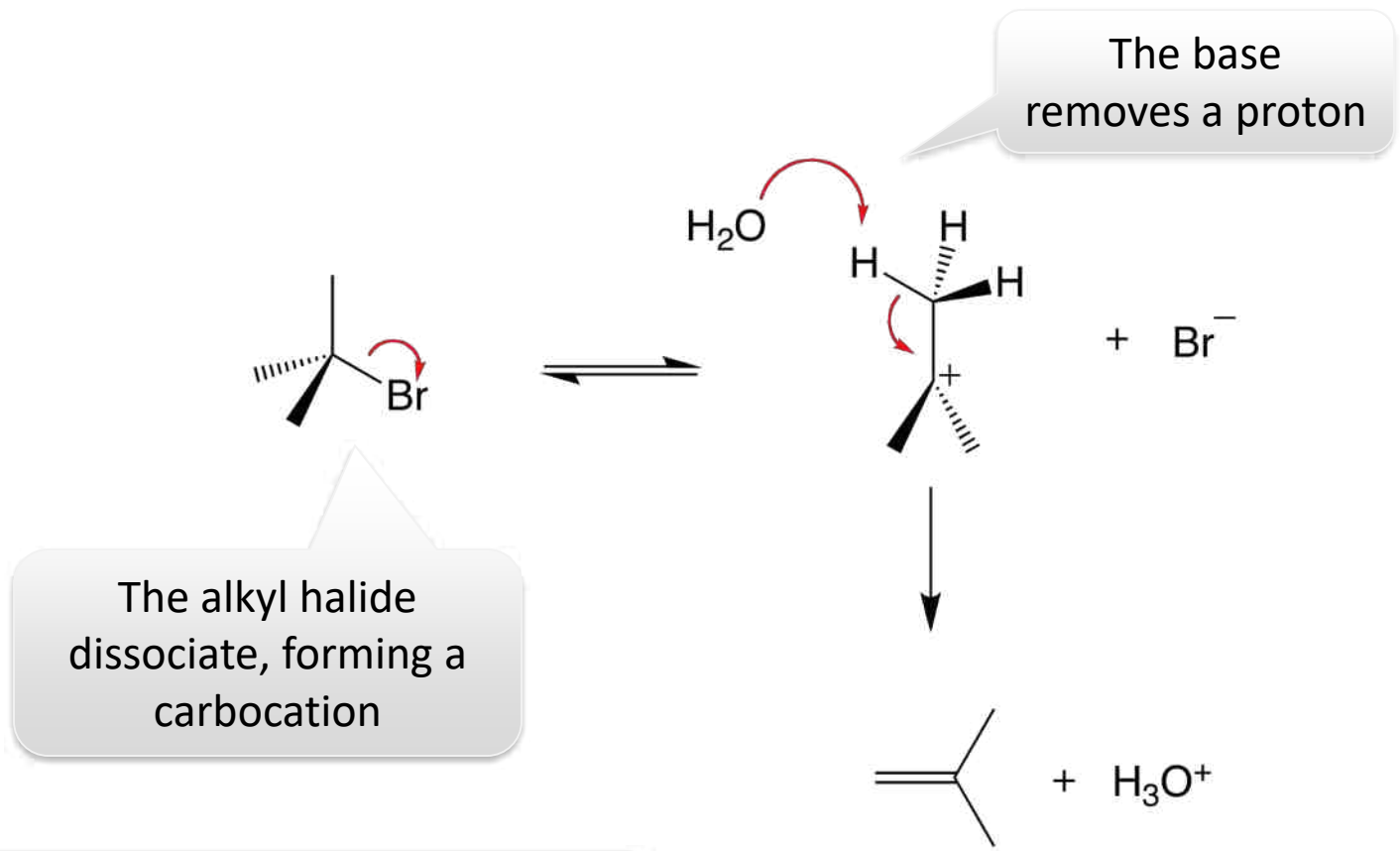
**E** stands for **elimination**

**2** stands for **bimolecular**

# The E2 Reaction

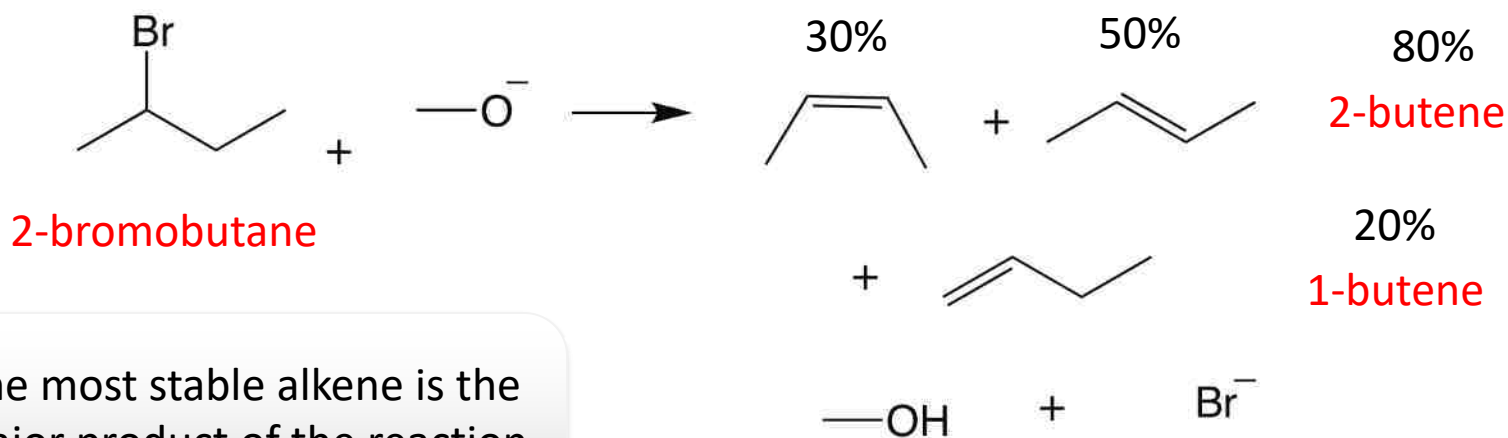


# The E1 Reaction



The mechanism shows that an E1 reaction is a two-step reaction

# Products of Elimination Reaction



The most stable alkene is the major product of the reaction for both E1 and E2 reaction

For both E1 and E2 reactions, tertiary alkyl halides are the most reactive and primary alkyl halides are the least reactive

The greater the number of alkyl substituent the more stable is the alkene

# Competition Between SN2/E2 and SN1/E1

SN1

SN2

E1

E2

$$\text{rate} = k_1[\text{alkyl halide}] + k_2[\text{alkyl halide}][\text{nucleo.}] + k_3[\text{alkyl halide}] + k_2[\text{alkyl halide}][\text{base}]$$

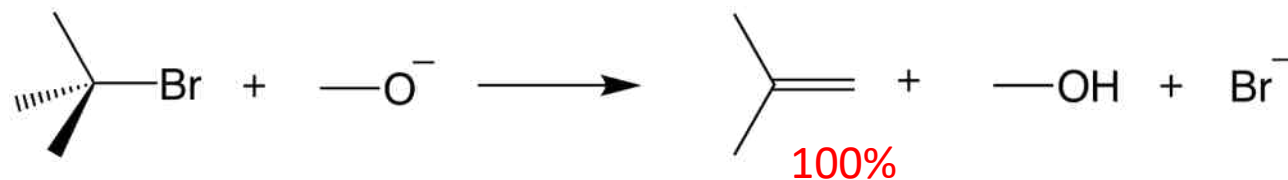
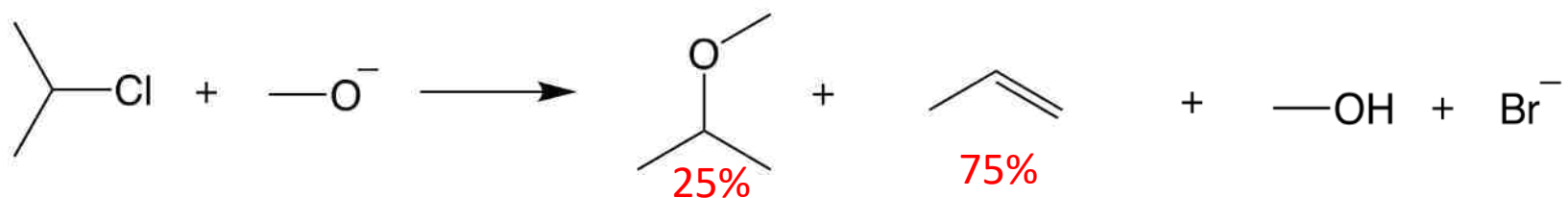
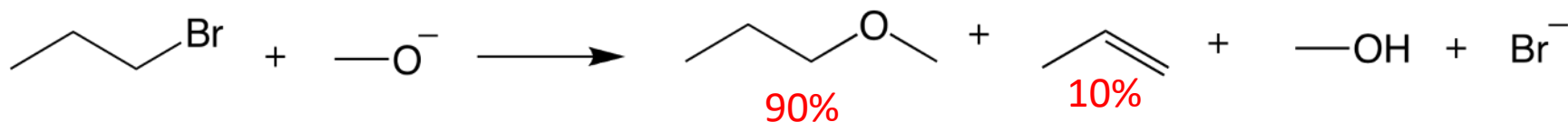
- SN2 and E2 are favoured by a high concentration of a good nucleophile/strong base
- SN1 and E1 are favoured by a poor nucleophile/weak base, because a poor nucleophile/weak base disfavours SN2 and E2 reactions

# Competition Between Substitution and Elimination

- SN2/E2 conditions:

In a SN2 reaction:  $1^\circ > 2^\circ > 3^\circ$

In a E2 reaction:  $3^\circ > 2^\circ > 1^\circ$



# Competition Between Substitution and Elimination

- SN1/E1 conditions:

All alkyl halides that react under SN1/E1 conditions will give both substitution and elimination products ( $\approx 50\%/50\%$ )