Corrosion of Iron

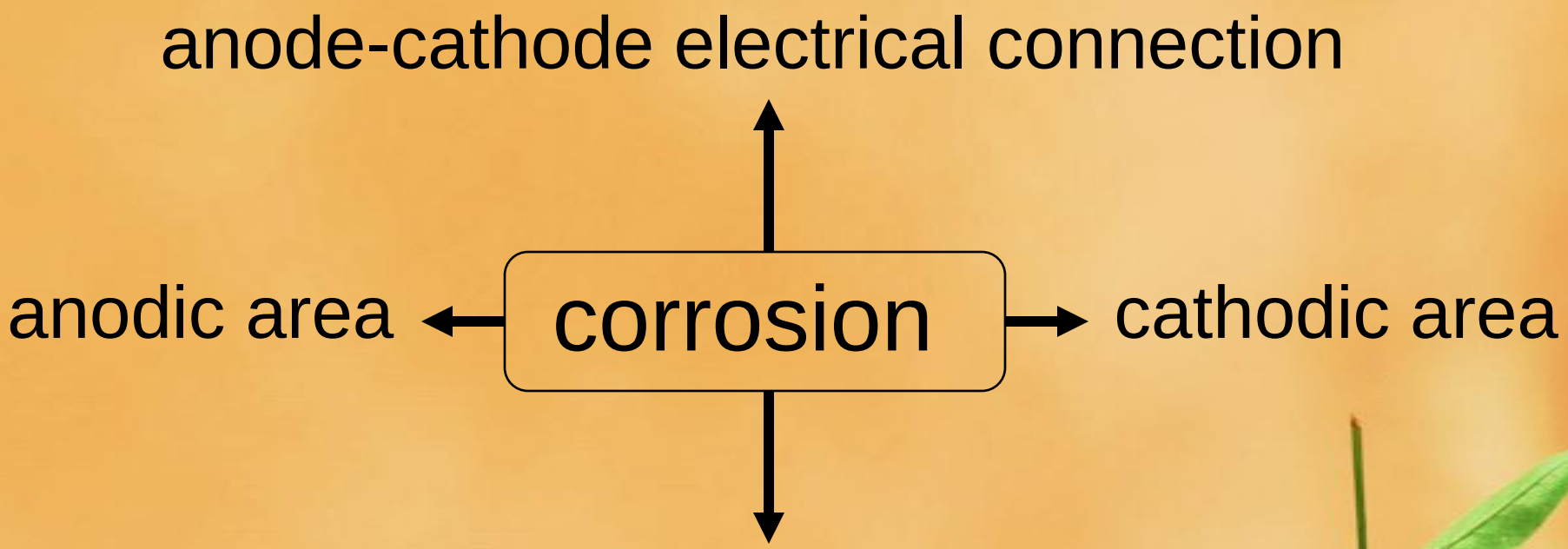
pranjoto utomo

Corrosion

- deterioration of metal caused by loss of metal to solution by oxidation - reduction reaction

- electron transfer

Corrosion



Corrosion

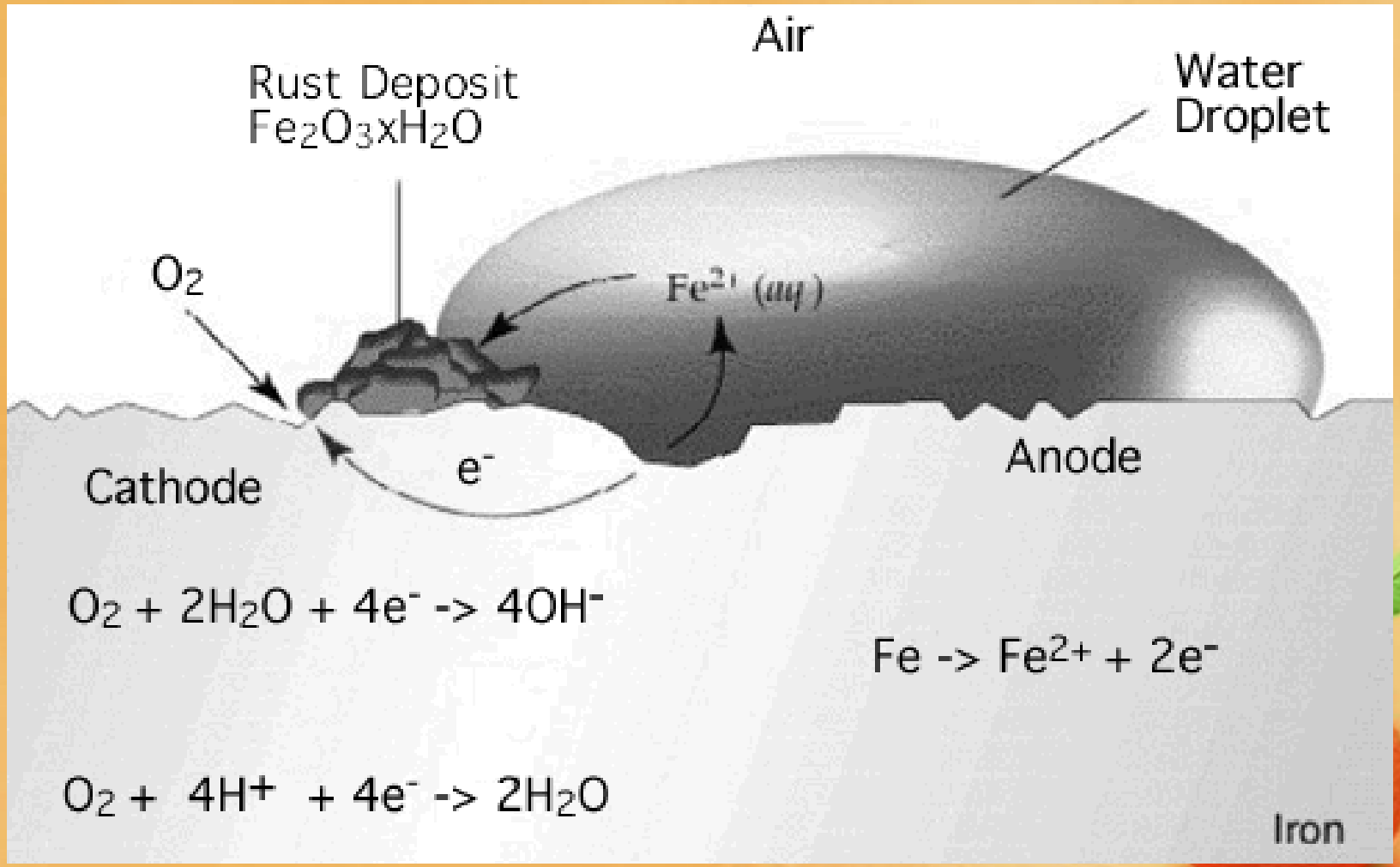
- Anodic area
  - Oxidation reaction
  - Crack in the oxides coating
  - Boundaries between phases
  - Around impurities

$$M \rightarrow M^{n+}(aq) + ne^-$$

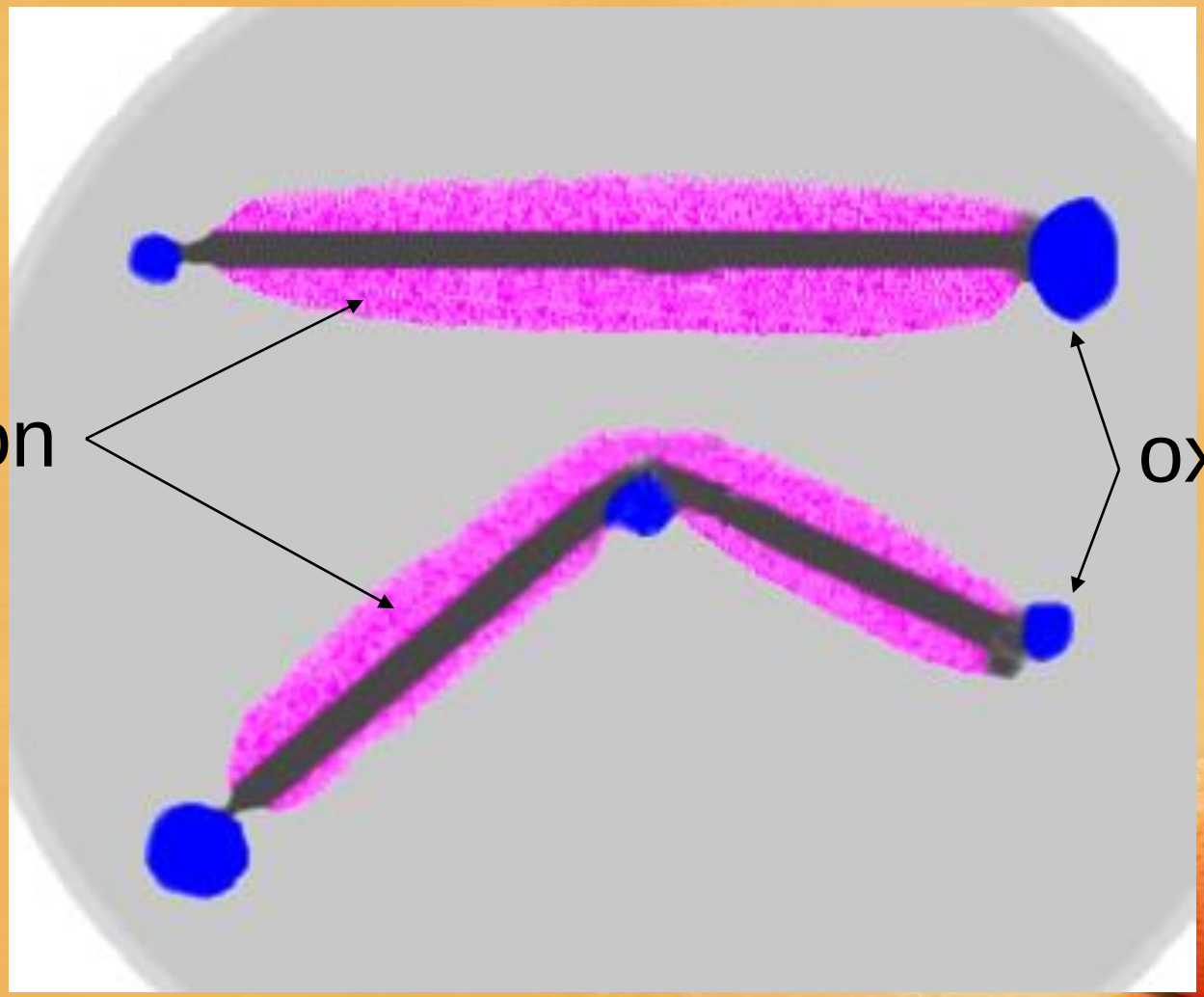
Corrosion

- Cathodic area
  - Reduction
  - Metal oxides coating
  - Less reactive impurities
  - Round other metal compound (sulfides)

The mechanism of the corrosion of iron



Corrosion of iron in gel medium



Corrosion of Iron

- rate of corrosion of anodic >> cathodic
- corrosion is controlled by cathodic process
- preventing

Corrosion of Iron

- anodic reaction :
  - oxidation of iron & electron are produced
  - $M\ (s) \rightarrow M^{n+} + n\ e^-$

Corrosion of Iron

- cathodic reaction :
  - depends on:
    - acidity of the surrounding solution
    - the amount of oxygen presence

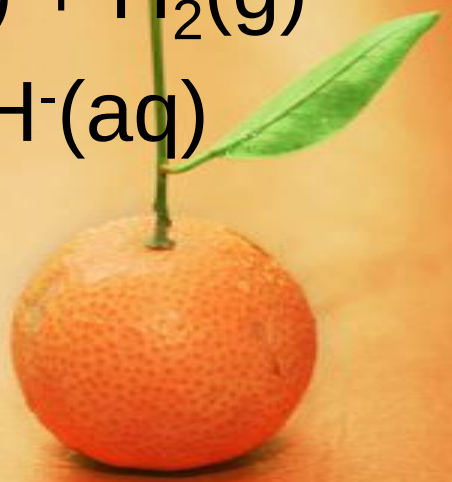
Corrosion of Iron

- cathodic reaction :
  - electron are consumed by any or all of several possible half reaction

$$2H^+(aq) + 2e^- \rightarrow H_2(g)$$

$$2H_2O(\ell) + 2e^- \rightarrow 2OH^-(aq) + H_2(g)$$

$$O_2 + 2H_2O(\ell) + 4e_- \rightarrow 4OH^-(aq)$$



Corrosion of Iron

1. in the absence (little) of free oxygen and H_2O

- e.g. iron nail buried in moist clay

- H_3O^+ & H_2O are reduced

Corrosion of Iron

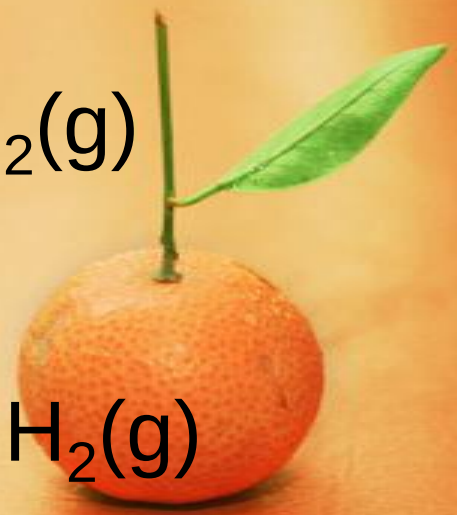
1. in the absence (little) of free oxygen and H_2O

- Reactions
  - anode:

    $Fe(s) \rightarrow Fe^{2+}(aq) + 2e^-$
  - cathode:

    $2H_2O(\ell) + 2e^- \rightarrow 2OH^-(aq) + H_2(g)$
  - net reaction:

    $Fe(s) + 2H_2O(\ell) \rightarrow Fe^{2+}(aq) + 2OH^-(aq) + H_2(g)$



Corrosion of Iron

1. in the absence (little) of free oxygen and water

   $Fe^{2+}(aq) + 2OH^{-}(aq) \rightarrow Fe(OH)_2(s)$

- $Fe(OH)_2$:
  - insoluble precipitate
  - precipitate on metal surface & inhibit further corrosion

Corrosion of Iron

1. in the absence (little) of free oxygen and water

- further oxidation of $Fe(OH)_2$

$$6Fe(OH)_2(s) + O_2(g) \rightarrow 2Fe_3O_4.H_2O(s) + 4H_2O(\ell)$$

green hydrated magnetite

Corrosion of Iron

1. in the absence (little) of free oxygen and water

- further reaction

$$Fe_3O_4.H_2O(s) \rightarrow Fe_3O_4(s) + H_2O(\ell)$$

black magnetite

- $Fe_3O_4(s)$ is rusted nail in moist soil

Corrosion of Iron

2. in the presence of oxygen and H_2O

- rate of corrosion 100 x faster than those without oxygen and water

Corrosion of Iron

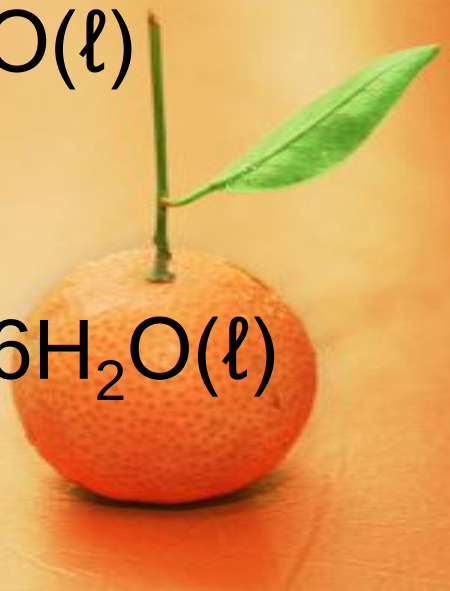
2.in the presence of oxygen and H_2O

- Reactions
  - anode:

    $2Fe(s) \rightarrow 2Fe^{2+}(aq) + 4e^-$
  - cathode:

    $O_2(g) + 4H_3O^+(aq) + 4e^- \rightarrow 6H_2O(\ell)$
  - net reaction:

    $2Fe(s) + O_2(g) + 4H_3O^+(aq) \rightarrow 2Fe^{2+}(aq) + 6H_2O(\ell)$



Corrosion of Iron

2.in the presence of oxygen and H_2O

- further oxidation of Fe^{2+} by $O_2 \rightarrow Fe^{3+}$

  $2Fe^{2+}(aq) + \frac{1}{2} O_2(g) + (6+x) H_2O(\ell)$

  $\rightarrow 2Fe_2O_3 . x H_2O(s) + 4H_3O^+(aq)$

  red brown

- $Fe_2O_3 \cdot xH_2O$: rust on car
- H_3O^+ : allow the corrosion cycle continue

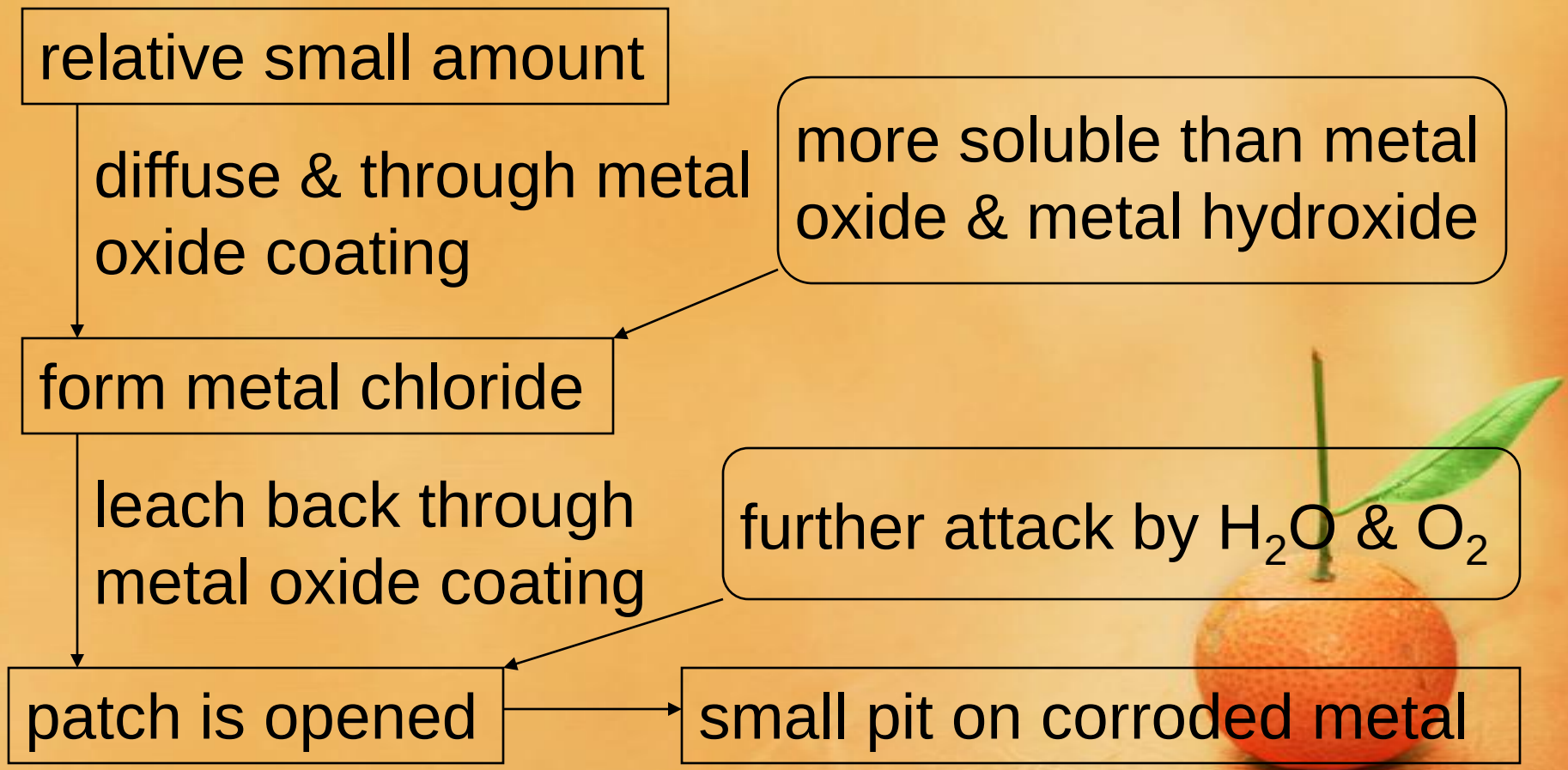
Corrosion of Iron

3. in the presence of chloride

   e.g. rapid rusting of car in salted water area

Corrosion of Iron

3. in the presence of chloride



Corrosion of Iron

4. in the presence of sulfur dioxide
   - formed in the combustion of oil and coal
   - 1300 times more soluble in water than O_2
   - oxidized to form sulfuric acid solution $\rightarrow$ acid rain

Corrosion of Iron

4. in the presence of sulfur dioxide

- redox reaction

$$Fe(s) + SO_2(g) + O_2(g) \rightarrow FeSO_4(s)$$

$$FeSO_4(s) + O_2(g) + 6H_2O(\ell) \rightarrow 2Fe_2O_3.H_2O(s) + 4H_2SO_4(aq)$$

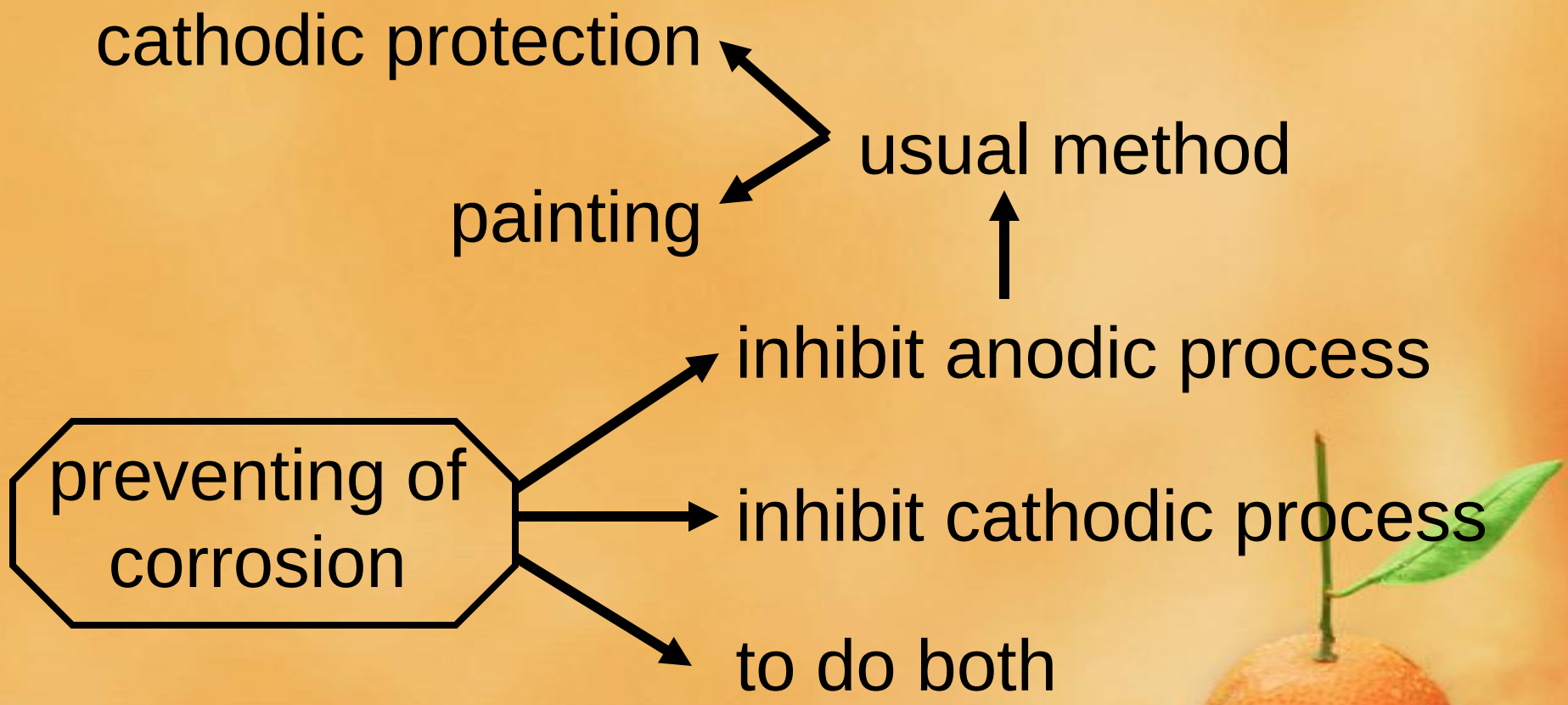
$$4H_2SO_4(aq) + 4Fe(s) + 2O_2(g) \rightarrow 4FeSO_4(s) + 4\ H_2O(\ell)$$

Corrosion of Iron

4. in the presence of sulfur dioxide

- H_2SO_4:
  - Once it produce, difficult to be removed
  - Allow corrosion continue

Corrosion of Iron



Painting

- formation of thin film of oxide
- prevent the oxidation half reaction of metal
- iron oxidized by Cr(II) salt to form Cr(VI) and Fe(III) oxides.

  $2\ Fe(s) + 2Na_2CrO_4(aq) + 2H_2O(\ell)$

  $\rightarrow Fe_2O_3(s) + Cr_2O_3(s) + 4NaOH(aq)$
- Cr_2O_3 protect iron for further oxidation by O_2 & water

Passivation

- to force the metal to become passive
- thin oxide layer formed on the surface
- prevent further electrochemical reaction

Passivation

- aluminum
  - with oxygen form aluminum oxides
- stainless steel
  - alloy of iron & chromium
- special design of paint
  - $K_2Cr_2O_7$ & Pb_3O_4
  - superficial oxidation & passivation of iron

Cathodic protection

- to force the metal to become the cathode in electrochemical cell
- attaching more readily oxidized metal
- e.g. galvanized iron (iron coated by zink) $\rightarrow$ sacrificial anode

?

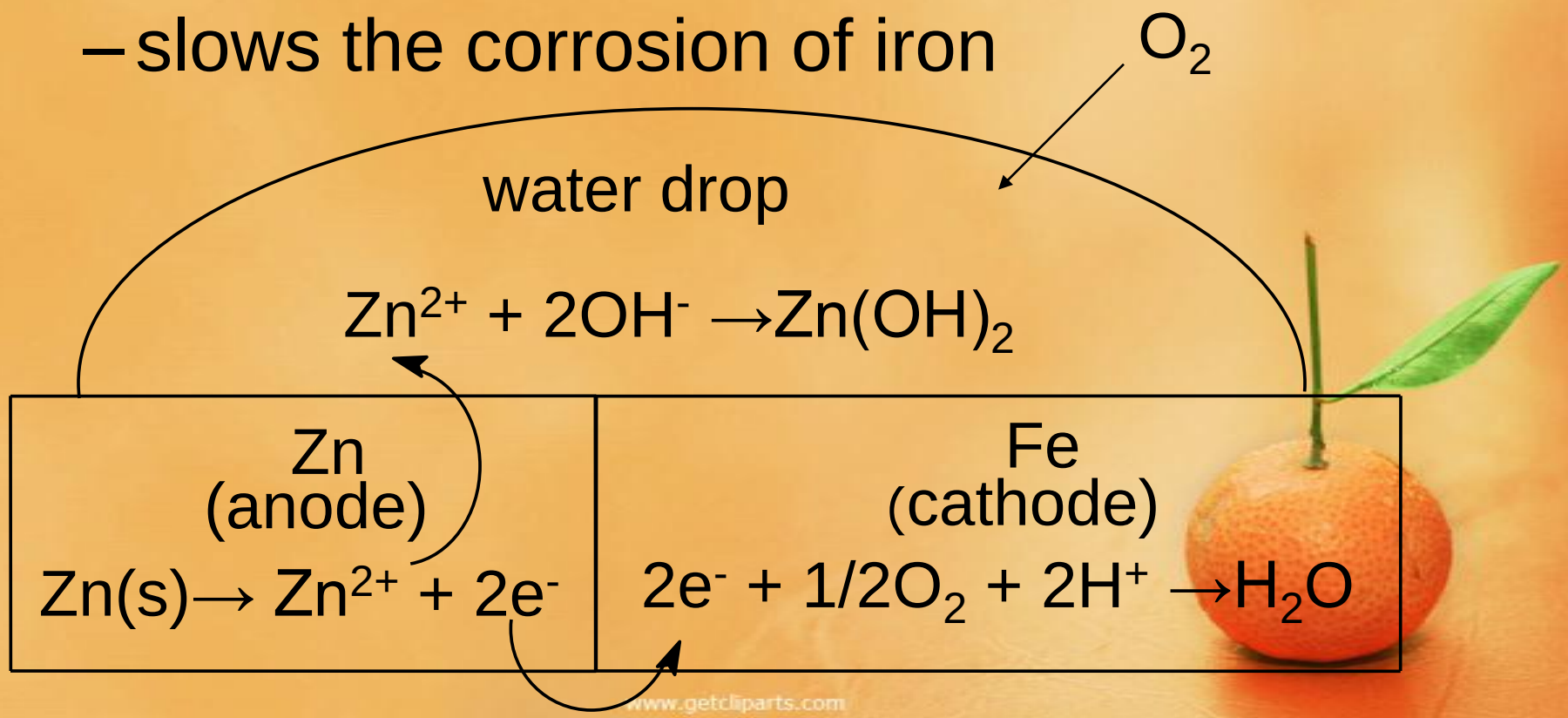
zink prevent corrosion of iron

Cathodic protection

- E^ored Zn < Fe or E^oox Zn > Fe
- Zn more readily oxidized than Fe
- Anodic :
  - $2Zn(s) \rightarrow 2Zn^{2+} + 4e^-$
- Cathodic :
  - $O_2 + 2H_2O(\ell) + 4e^- \rightarrow 4OH^-(aq)$
- Redox :
  - $2Zn(s) + O_2 + 2H_2O(\ell) \rightarrow 2Zn(OH)_2(s)$

Cathodic protection

- $Zn(OH)_2(s)$:
  - less soluble than $Fe(OH)_2$
  - slows the corrosion of iron



Mg used to prevent corrosion of iron in:

- buried pipe
- ship hulls
- bridges

Mg