KSU CET UNIT

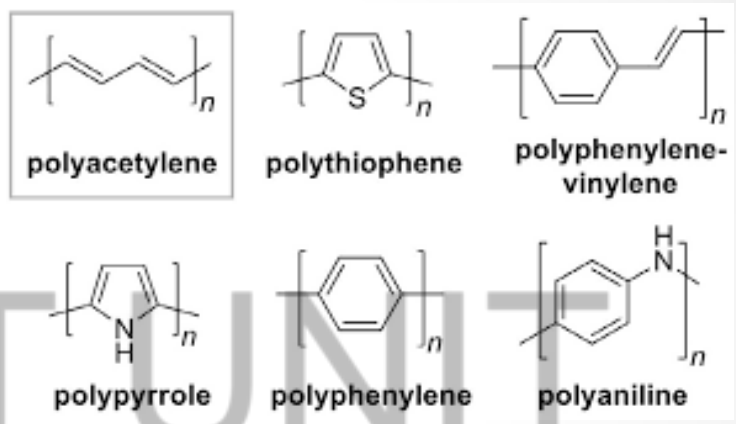
FIRST YEAR NOTES

CET UNIT

What are Conducting Polymers?

- Generally polymers are insulators.
- But certain polymers have been developed which can conduct electricity. They are called **conducting polymers**.

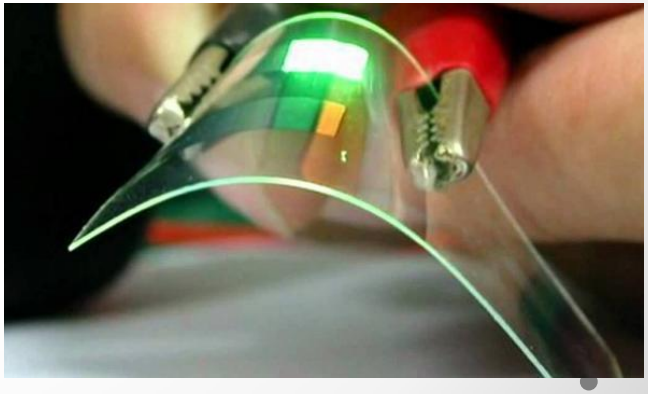
eg: Poly acetylene, polyaniline, poly pyrrole.



What makes conducting polymers so important?

Chemical properties- ion transport possible, redox behavior, Catalytic properties, electrochemical effects, photoactivity etc.

Mechanical properties- light weight, flexible, non metallic surface properties etc.



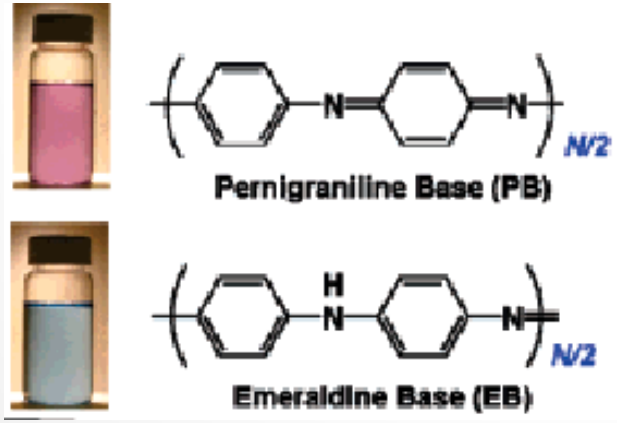
History

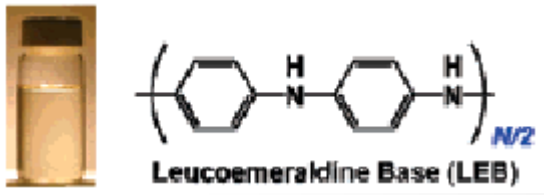
- **Organic molecules were previously considered as insulators or at best weakly conducting semiconductors except charge transfer complexes.**

- **The first highly-conductive organic compounds were the charge transfer complexes. In the 1950s, researchers reported that polycyclic aromatic compounds formed semi-conducting charge-transfer complex salts with halogens.**

- **Polyaniline was first described in the mid-19th century by Henry Letheby who investigated the electrochemical and chemical oxidation products of aniline in acidic media. He noted that reduced form was colourless but the oxidized forms were deep blue.**

- Polyaniline can be found in one of three idealized oxidation states.



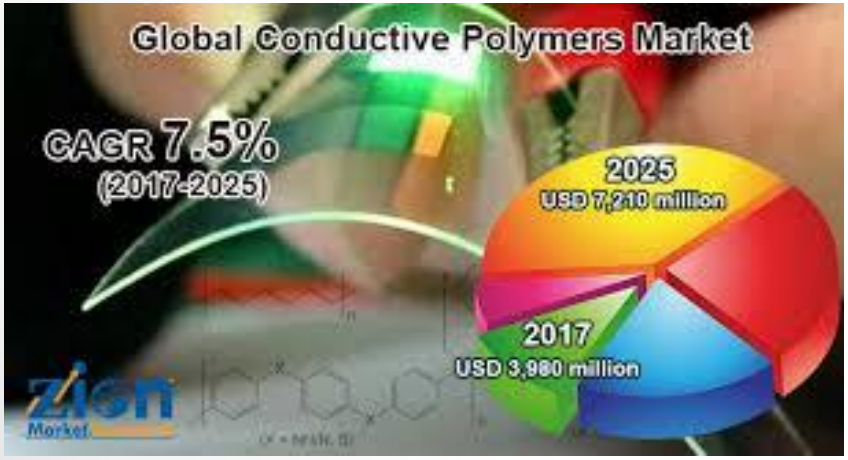


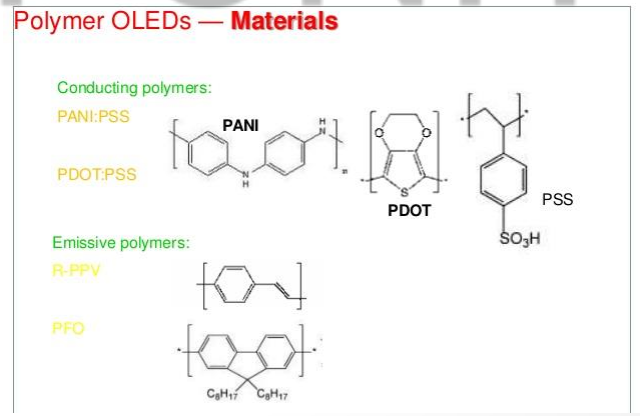
History

- In 1963 Australians B.A. Bolto, D.E. Weiss, and coworkers reported derivatives of polypyrrole with resistivities as low as 1 ohm·cm.

- In the early 1970s, researchers demonstrated salts of tetrathiafulvalene show almost metallic conductivity, while superconductivity was demonstrated in 1980.

- In 1977, Alan J. Heeger, Alan MacDiarmid and Hideki Shirakawa reported similar high conductivity in oxidized iodine-doped polyacetylene. For this research, they were awarded the 2000 Nobel Prize in Chemistry *"for the discovery and development of conductive polymers.*





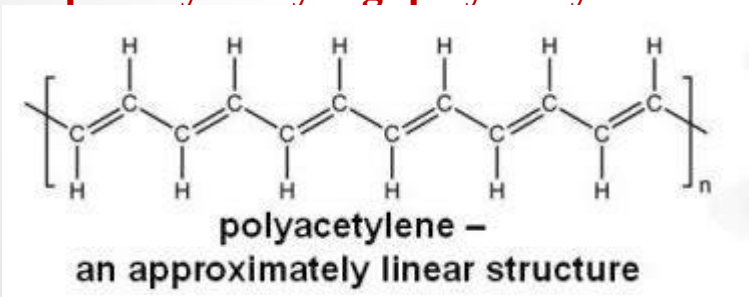
Since the late 1980s, organic light-emitting diodes(OLEDs) have emerged as an important application of conducting polymers.

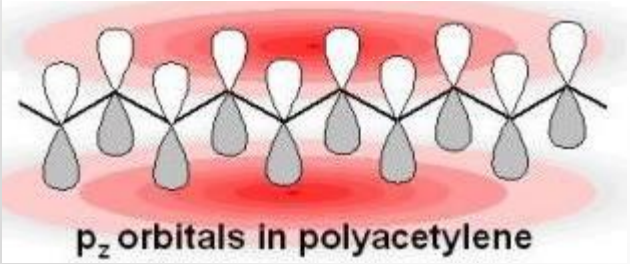
Theory of conductance in conducting polymers

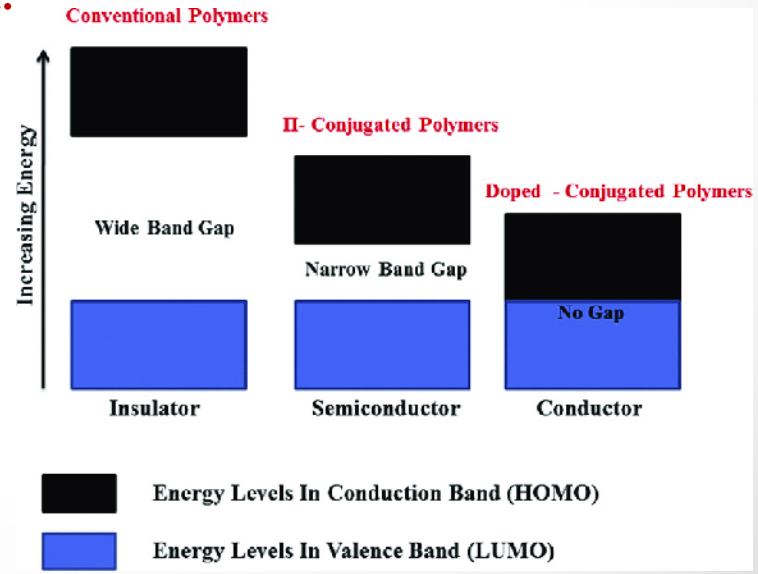
- In traditional polymers such as polyethylenes, the valence electrons are bound in sp^3 hybridized covalent bonds. Such "sigma-bonding electrons" have low mobility and do not contribute to the electrical conductivity of the material.

- However, in conjugated materials, the situation is completely different.

- Conducting polymers have backbones of continuous sp^2 hybridized carbon centers. One valence electron on each center resides in a p_z orbital, which is orthogonal to the other three sigma-bonds. All the p_z orbitals combine with each other to a molecule to form valence bands and conductance bands. Highest occupied band is called the valence band and the and lowest unoccupied band is called the conductance band. These bands are separated by a band gap. Electrical conductance occur when electron from valence band are excited to conduction band thermally or photolytically. Eg: poly acetylene and polyaniline.

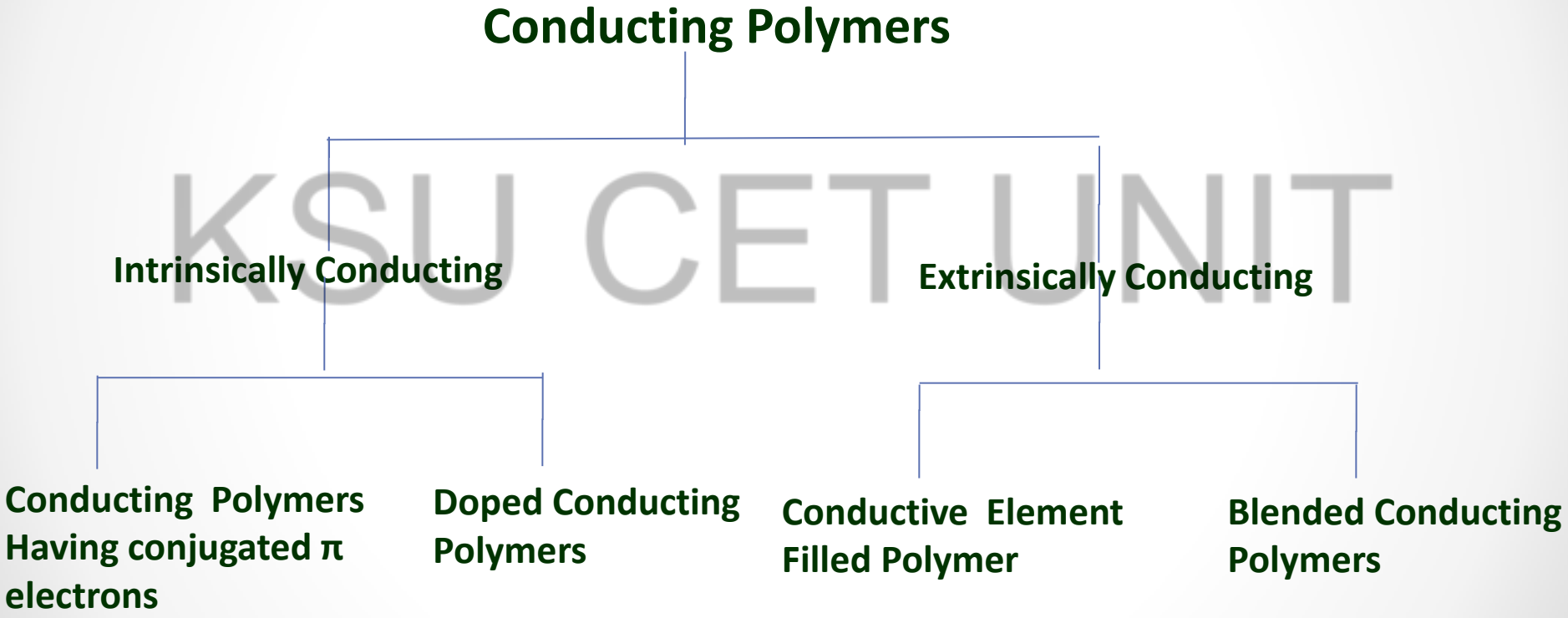






Different Conducting Polymers

Conducting polymers can be classified into following types



Intrinsically Conducting Polymers (ICP)

The conduction of electricity in this type of polymers is due to conjugated double bonds along the backbone of the polymer. This is again classified as

a) Conjugated π electron conducting polymers

These are simple ICP which we disscussed in the previous slides.

eg: polyacetylene, polyaniline.

b) Doped conducting polymers

These are ICPs whose onductivities can be increased by creating positive or negative charges on polymer backbone by oxidation or reduction thereby increasing the mobility of these electrons in these delocalized orbitals. This process is called doping.

Doped Conducting Polymers

- ✓ So far we have seen, the conduction of electricity in ICP is due to conjugated double bonds along the backbone of the polymer where the orbital's of the conjugated π electron overlaps over the entire backbone of the polymer resulting in the formation of valence bands and conductance bands.
- ✓ Hence ICP can be easily oxidized or reduced as they have low ionization potential and high electronic affinities.
- ✓ ie, Conductivities can be increased by creating positive or negative charges on polymer backbone by oxidation or reduction thereby increasing the mobility of these electrons in these delocalized orbitals. This process is called doping.

Doped Conducting Polymers

Undoped conjugated polymers, such as polythiophenes, polyacetylenes etc, only have a low electrical conductivity of around 10^{-10} to 10^{-8} S/cm. Even at a very low level of doping (< 1%), electrical conductivity increases several orders of magnitude up to values of around 0.1 S/cm. Subsequent doping of the conducting polymers will result in a saturation of the conductivity at values around 0.1–10 kS/cm for different polymers.

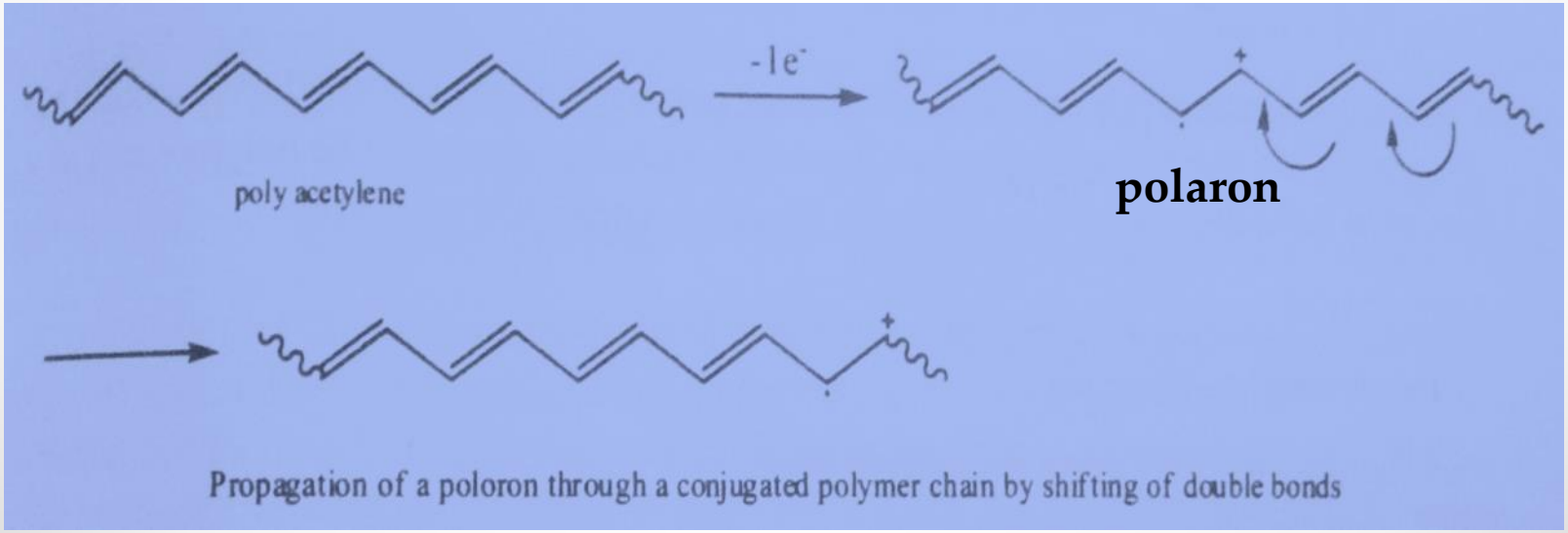
The role of a dopant is to either add or remove electrons to the polymer. It is of two kinds.

1. **Oxidative or p-doping**
2. **Reductive or n-doping**

Oxidative or p-doping

• **Done by oxidation process. In this process some electrons from π bond of the conjugated double bonds are removed and holes are created. This radical cation produced is called Polaron.**

•**Polarons are mobile and can move along the polymer chain by rearrangement of double & single bonds and hence the poymer becomes conducting. The oxidation is generally brought about by Lewis acids such as $FeCl_3$.**

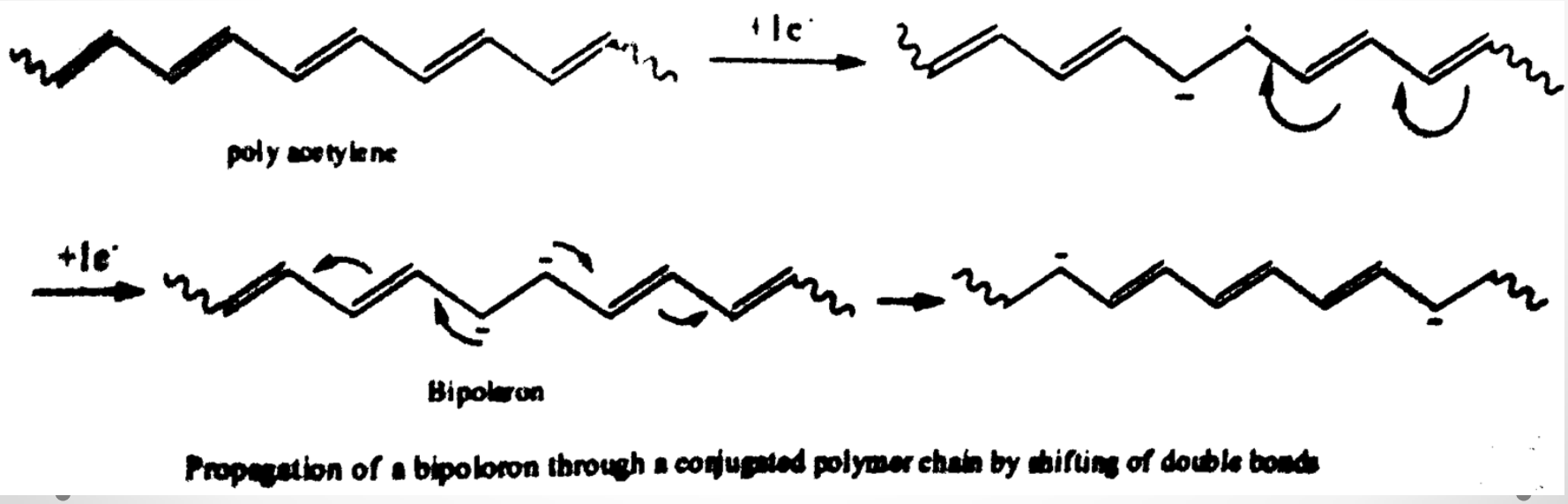


Propagation of a poloron through a conjugated polymer chain by shifting of double bonds

Reductive or n-doping

In this type of doping some electrons are introduced into the polymer having conjugated double bonds by reduction with Lewis bases like sodium naphthalide.

The reduction of polyacetylene by a lewis base leads to the formation of a polaron and bipolaron in two steps.



Propagation of a bipoloron through a conjugated polymer chain by shifting of double bonds

Extrinsically conducting polymers

These are conducting polymers whose conductivity is due to externally added ingredients such as

(a) Conductive element filled polymer

These are polymers filed with conducting elements such as carbon black, metallic fibres, metal oxides etc. The polymer acts as a binder to hold the conducting elements together. These polymers are;

1. Low in cost 2. Light in weight 3. Mechanically durable and strong

4.Easily processable in different forms, shapes and sizes

But addition of fillers reduces the tensile strength, impact strength etc of these polymers

(b) Blended conducting polymers

Obtained by blending conductive polymers with conventional polymers.

These polymers posses better physical, chemical and mechanical properties.

Applications of Conducting polymers

1. In rechargeable Batteries:

The CPs can be used as cathodes and solid electrolytes in batteries for automotive and other applications.

- **Advantages**
  - **light weight and are small in size.**
  - **Longer cyclic time.**
  - **High discharge time.**
  - **Less self discharge time.**
  - **Non leakage of electrolytic.**
  - **Flexible shape and easy fabrication of component in film form.**
- **Disadvantages**
  - **cost**

Applications of Conducting polymers

2. One of the important application of CPs are OLED displays like TV, mobile phones etc.
3. ICPs like polyaniline show different colours in different oxidation forms. This electrochromic property can be used to produce “Smart Windows” and electrochromic displays.
4. In analytic sensors: these polymers are used for making sensors for pH, O_2, SO_2, glucose etc.