Announcement

written exam

Saturday, January 31, $15^{15} – 18^{15}$

CO 2

up to 12 multiple-choice questions (only one answer is correct)

1. Which of the following reactions is a polycondensation?
   a) Reaction of an epoxy resin with a diamine in a closed mold. ☐
   b) Reaction of a diisocyanate with a diol in the presence of water to form a foamed polyurethane. ☐
   c) Ring opening polymerization of caprolactam to form polyamide 6. ☐
   d) Radical polymerization of ethylene to form polyethylene. ☐

2. For an amorphous polymer of high molar mass, $C_\infty = 9$ and the maximum deformability of the entanglement network, $\lambda_{max} = 4$. What is the average number of bonds between two entanglement points?
   a) 20 ☐
   b) 36 ☐
   c) 81 ☐
   d) 144 ☐

4 out of 6 longer questions need to be answered

1. The melting temperature of a crystalline lamella formed by a polymer is given by

$$T_m = T_{m0}\left(1 - \frac{2\sigma_e}{l\Delta H}\right)$$

   a) Explain the meaning of the different terms in this equation with reference to a schematic representation of a lamella, and thus explain its physical origin.

   b) In a semi-crystalline polymer, the lamellae are organized in the form of spherulites. What is a spherulite and what are the mechanisms that lead to the formation of spherulites from lamellar nuclei within a molten polymer when $T_g < T < T_{mo}$?

   c) During injection molding, a highly stretched molten polymer comes into contact with the walls of a cold mold. What are the consequences for its morphology? (Assuming that the polymer is able to crystallize.)

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Polymer Technology

6.1 From Oil to Base Chemicals

The Chemical Industry

- the branch of chemistry applying physical and chemical procedures towards the transformation of natural raw materials and their derivatives to commercial products that are of benefit to humanity

example: BASF Ludwigshafen
10 km^2
2000 buildings
106 km streets
230 km railways

- **strong dependence on raw materials and their (local) availabilities**
- **dynamic: reactive on market pressures due to strongly interrelated technological processes**

World Chemical Market 2024

- **the backbone of the chemical industry**: dominated by a few large-volume base inorganic and organic precursors to mainstream plastics

chemical	production (million metric tonne)	primary use
sulfuric acid	261	fertilizers
ammonia	195	fertilisers
ethylene	177	plastics
propylene	160	plastics
nitrogen	≈ 100	fertilisers
chlorine	97	water treatment, plastics
oxygen	≈ 80	steel
sodium hydroxide	≈ 80	healthcare
ethylene dichloride	45	plastics
phosphoric acid	42	fertilizers

- **the majority of the remaining chemicals in the top 50 are organic (referred to as petrochemicals)**

Where Do Industrial Organic Chemicals Come From?

- major sources: petroleum (crude oil) and natural gas (almost entirely methane)

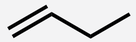
methane

CH_4

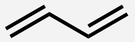
ethylene

propylene

C_4 olefins
(butenes, butadiene)



1-butene



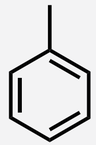
cis-2-butene

trans-2-butene

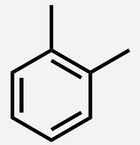
2-methyl-1-propylene

benzene

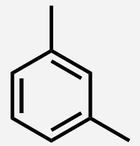
toluene



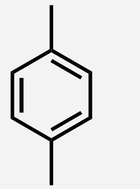
xylenes



o-xylene



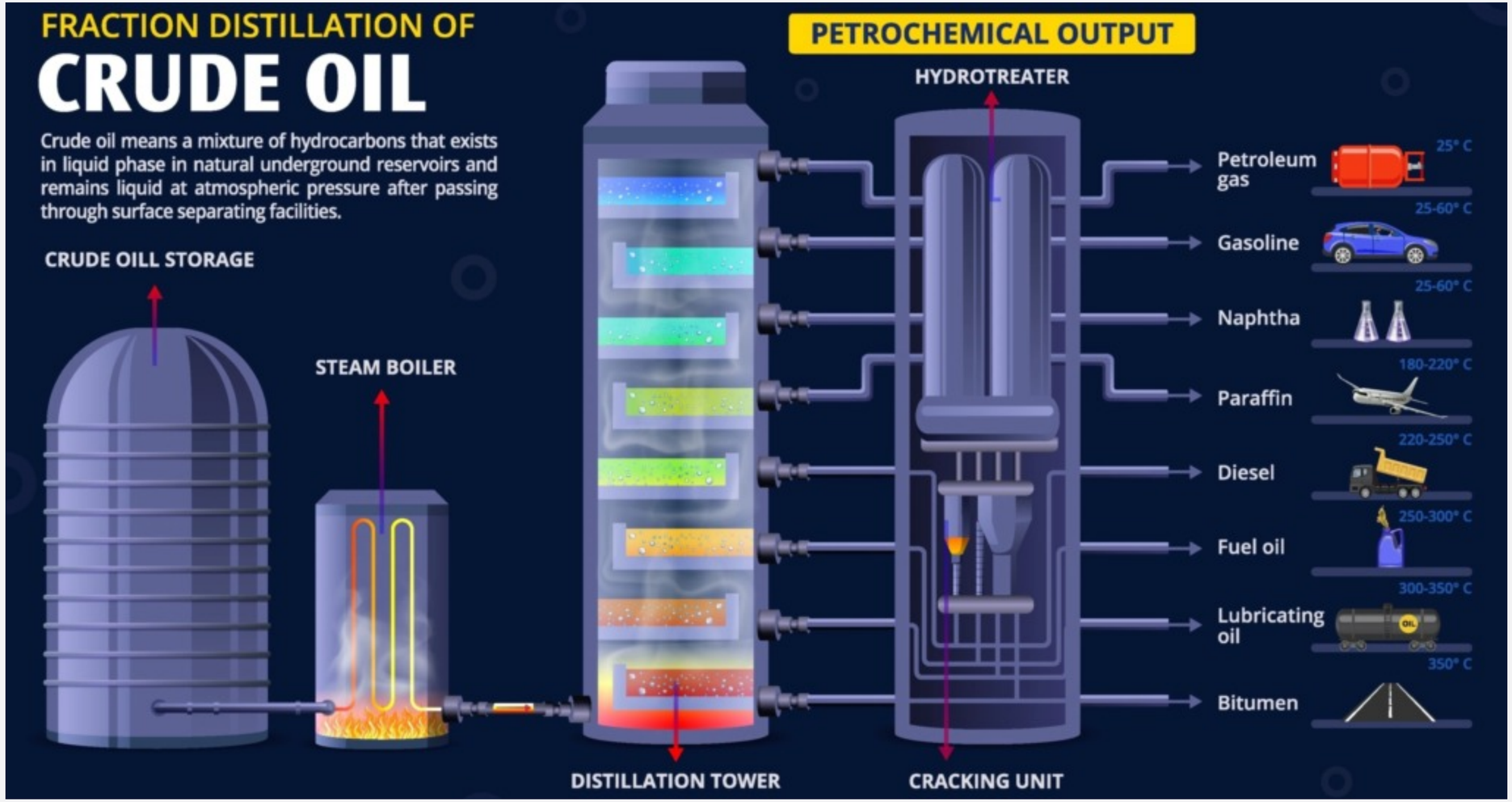
m-xylene



p-xylene

- **7 major building blocks of the petrochemical industry**
- moreover: coal, natural products (triglycerides, carbohydrates, sterols, alkaloids, phospholipids

Crude Oil Distillation

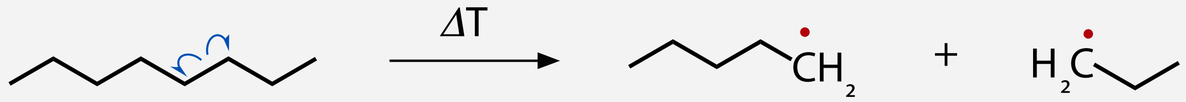


- **naphtha fraction is of particular importance to the chemical industry**
- **competition between fuel oil** (light naphtha = straight run gasoline) **and petrochemical production**

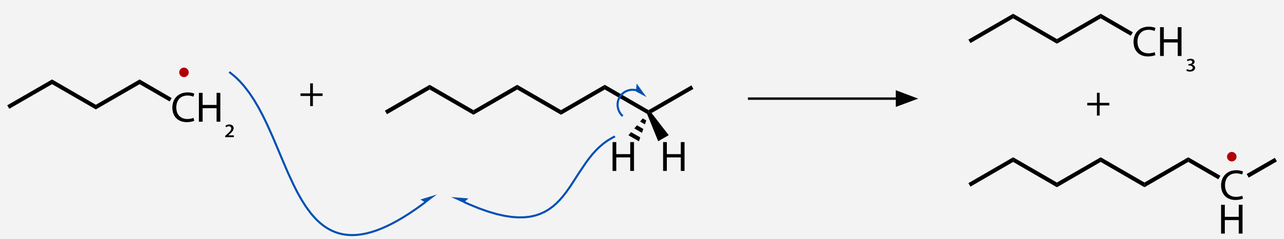
Chemical Conversion Processes

- **petroleum refining reactions:** catalytic reforming, oligomerization, alkylation, hydrotreating and coking dehydrogenation, isomerization, metathesis

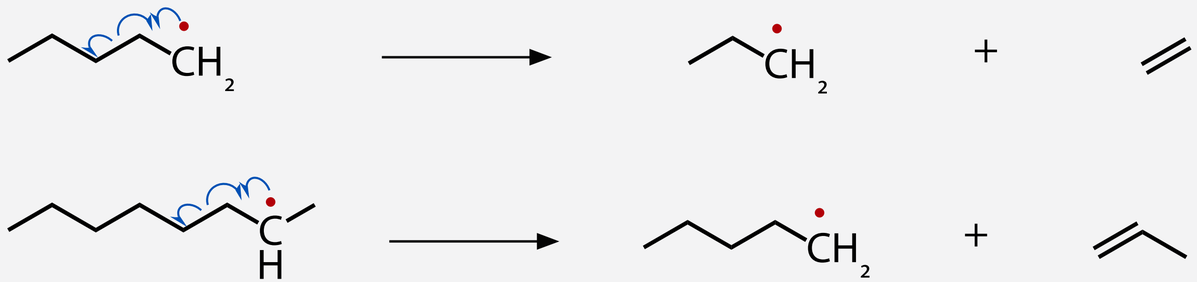
homolysis



hydrogen abstraction



β-abstraction

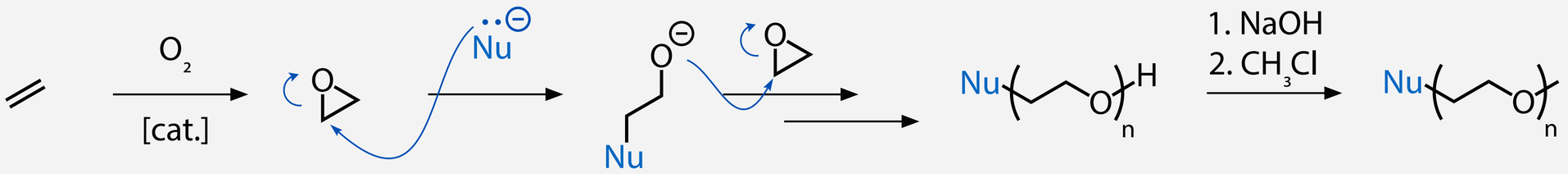


hydrocarbon	road index octane number
heptane	0
ammonia	23
hexane	25
2-methylhexane	44
1-heptene	60
pentane	62
1-pentene	84
butane	91
cyclohexane	97
isooctane	100
benzene	101
toluene	112

- **steam cracking (fully petrochemicals targeted) leads to high proportion of olefins at high temperatures**

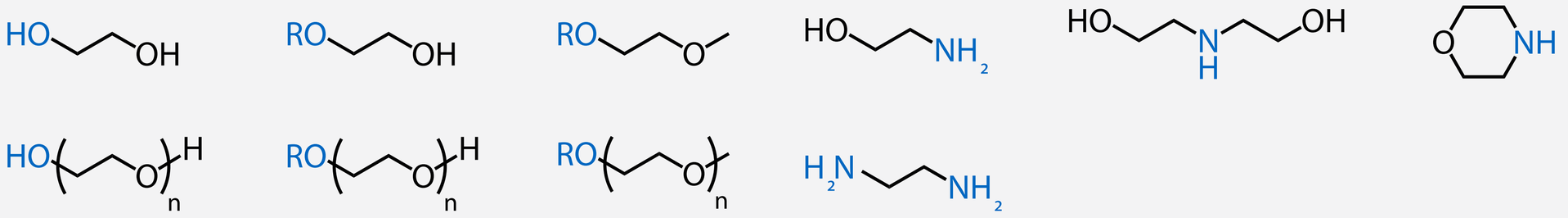
Chemicals and Polymers from Olefins

- ethylene: the most important organic base chemical



Nu: H_2O, ROH, NH_3

industrial intermediates/products:

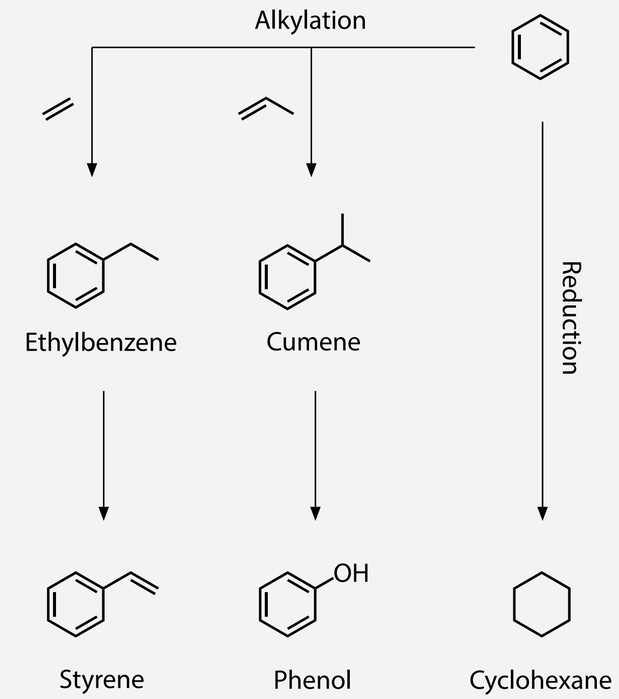


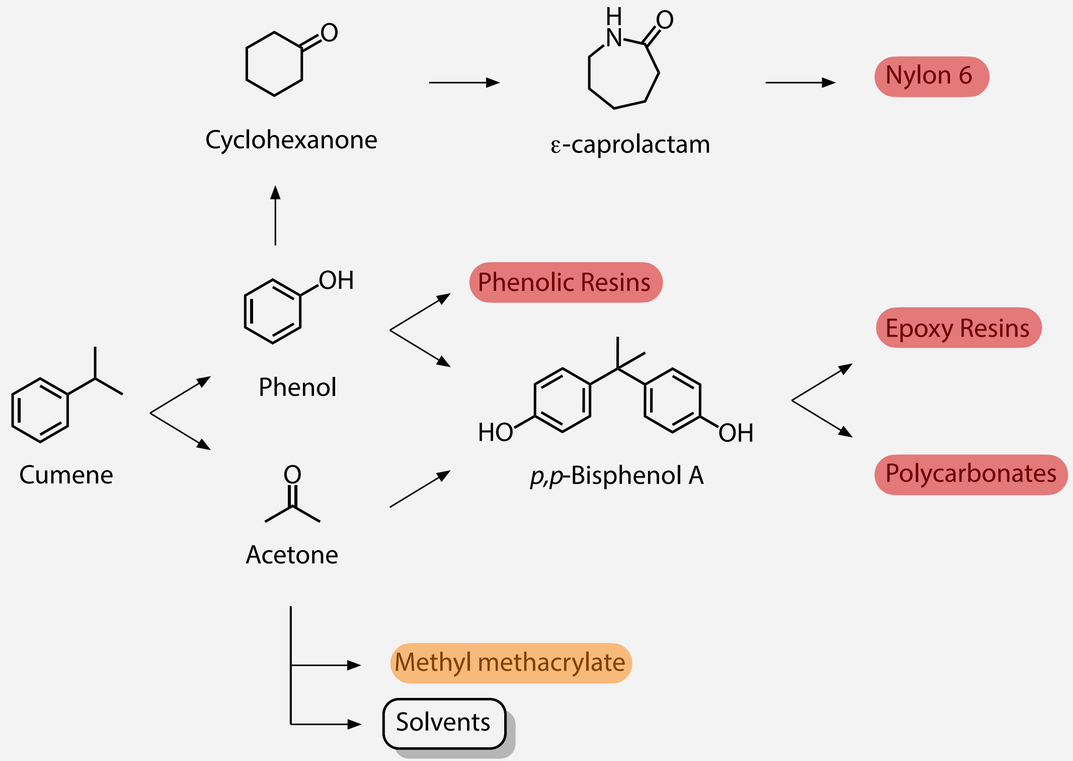
- **monomer synthesis for polymers** (styrene, vinyl chloride, ethylene glycol, …)
- **precursor to various lower volume chemicals** (propionic acid, acetaldehyde, ethylenediamine, …)
- similar for propylene (used for polypropylene, propylene oxide, acrylonitrile, …)

Chemicals from Benzene

- **benzene: 3rd most important organic base chemical, precursor of various aromatic intermediates**
- example: cumene is the basis for an extensive value chain towards polymer precursors and polymers

the top three chemicals accounting for 75 - 90% of global benzene consumption:





- toluene, xylenes: higher octane number and lower toxicity favour their use in unleaded gasoline

Overview on Base Chemical Production

- from a few base chemicals to polymer precursors and polymers