T7. Nitrogen Fixation

7%							
7.1	7.2	7.3	7.4	7.5	7.6	7.7	$\sum$
3	8	15	3	6	6	13	54

The Haber–Bosch process is the principal industrial method for ammonia production. A simplified diagram of an ammonia synthesis plant is shown below.

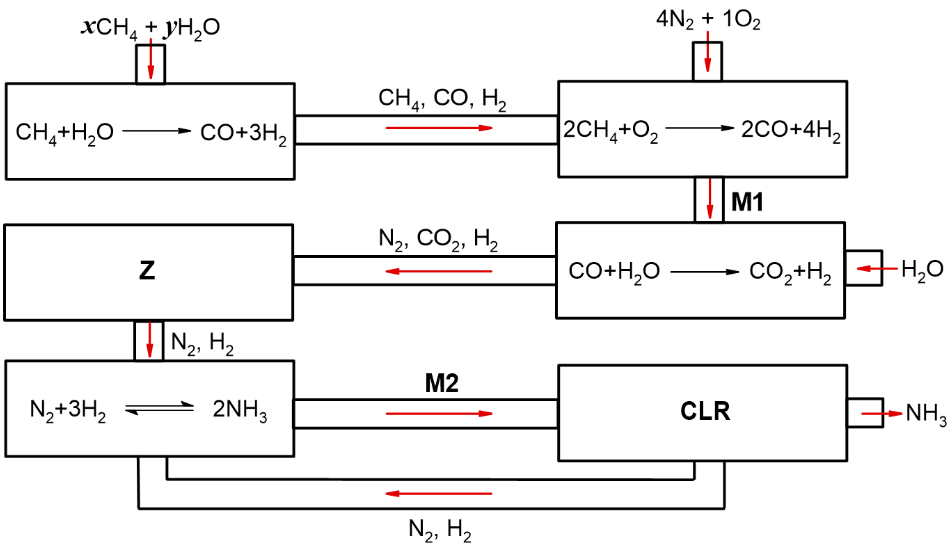


Fig. 1. **M1** - Mixture 1, **M2** - Mixture 2, **Z** – CO_2 scrubber, **CLR** - cooler

In the following calculations, assume that all reactions in **Fig. 1**, except NH_3 formation, are quantitative.

7.1	**Tick** the gases contained in **M1** and **M2**; and **tick** the correct relationship between x and y.	3.0 pt

An ammonia production complex with a capacity of $660,000$ tons per year was commissioned at the *Navoiazot* plant in Uzbekistan, which operates with a 97.0% of overall yield.

7.2	**Calculate** the mass of CH_4 (tons) required annually to produce $660,000$ tons of ammonia, if the *Navoiazot* operates according to the **Fig. 1**.	8.0 pt

Consider a model of a real reaction system, which includes recirculation of reagents. An open system operates in a cyclic mode. Each cycle consists of four steps:

1. A stoichiometric $N_2 : H_2 = 1 : 3$ mixture with a total amount of n_0 mol is fed into the reactor after each cycle.
2. The reaction proceeds with a constant yield of $\eta = 0.150$.
3. Ammonia is separated by liquification.
4. Unreacted gases are returned into the reactor.

The cycle is repeated until the required overall yield is reached.

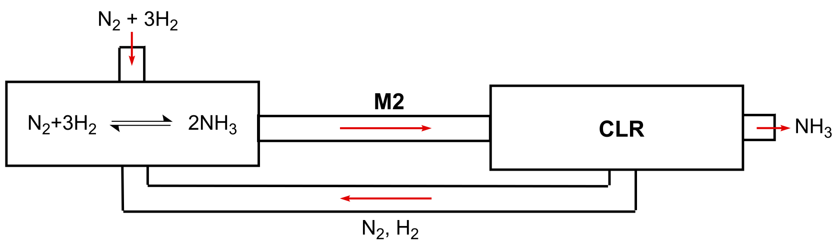
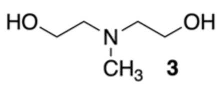


Fig. 2. M2. – Mixture 2, **CLR** - cooler.

7.3	a) **Calculate** the amount of nitrogen, present in the system after the 58th cycle (before the addition of 59th portion of mixture), if $n_0 = 4$ mol. **Provide** 4 decimal places. *Hint: a formula for the sum of the terms of a geometric progression is needed.* b) **Calculate** the number of cycles needed to increase the **overall** yield from 15.0% to 97.0%.	15.0 pt

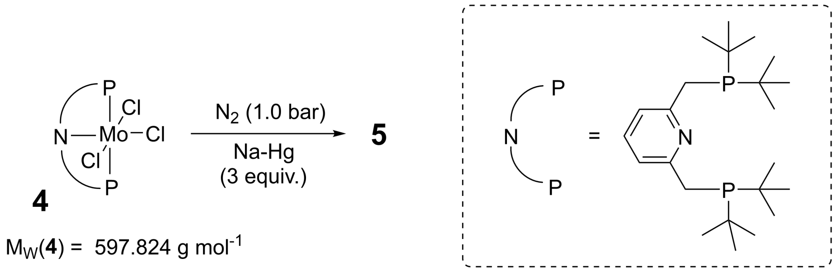
An aqueous solution of **3** is being used to remove CO_2 from the mixture.



3

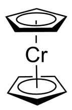
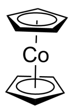
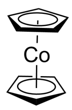
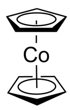
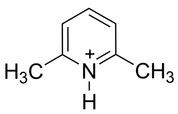
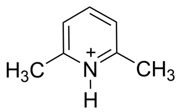
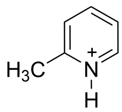
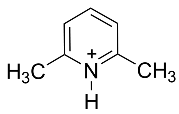
7.4	**Write** the equation for this reaction.	3.0 pt

Complex **5** is obtained through the fixation of the molecular nitrogen according to the scheme below.

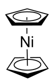
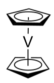
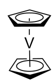
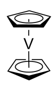
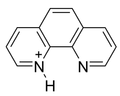
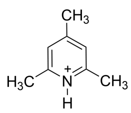
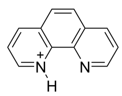
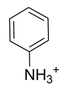


7.5	**<u>Draw</u>** the structure of **5** using simplified scheme for the ligand. Note that 1.00 g of **4** will react stoichiometrically with 94.97 cm^3 of N_2 at 273.15 K and 1.0 bar.	6.0 pt

The effect of different reductants and additives on the yield of NH_3 was examined. The different Red and Ad combinations, their respective *E*° and pK_a, together with the resulting NH_3 yield are presented below.

#	**1**	**2**	**3**	**4**
Red				
E° (V)	-0.88	-1.15	-1.15	-1.15
Ad	 $CF_3SO_3^-$	 Cl^-	 $CF_3SO_3^-$	 $CF_3SO_3^-$
pK_a	14.4	14.4	13.9	14.4
NH_3 yield (mole)	0	0.7	9.1	11.8

7.6	**Rank** the following **Red/Ad** combinations **A-D** by the decrease in ammonia yield.	6.0 pt

#	A	B	C	D
Red				
$E°$ (V)	-0.09	-1.10	-1.10	-1.10
Ad	 $CF_3SO_3^-$	 $CF_3SO_3^-$	 $CF_3SO_3^-$	 $CF_3SO_3^-$
pK_a	13.7	15.0	13.7	10.6

Nitrogen fixation can also be achieved via binary nitrides (compounds containing N^{3-}). Such nitrides **7**, **8**, **9** were obtained from pure elements. When they are heated together with SiO_2, red crystals of a stable compound **10** are formed as the single product. The minimal possible formula, describing the structure of compound **10** is $\mathbf{Q}_\alpha\mathbf{R}_\beta\mathbf{S}_2\mathbf{T}[Si_{12}N_{24}]$. In addition:

1. Mass fractions of nitrogen are $w(N)_\mathbf{7}$ =9.16%, $w(N)_\mathbf{8}$ =18.90%, $w(N)_\mathbf{9}$ =39.94%
2. **Q** and **R** are metal cations in their highest oxidation state.
3. **S** is a monoatomic anion.
4. **T** is an anion with tetrahedral configuration.
5. For the quantitative formation of **10**, the mass ratio **7** : **8** : **9** : SiO_2 = 5.09 : 2.96 : 3.27 : 1.00.

7.7	**Identify** the empirical formulae of **7 – 10**. **Specify** the composition of anions **S** and **T**.	13.0 pt