T7. Nitrogen Fixation

7%							
7.1	7.2	7.3	7.4	7.5	7.6	7.7	Σ
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.

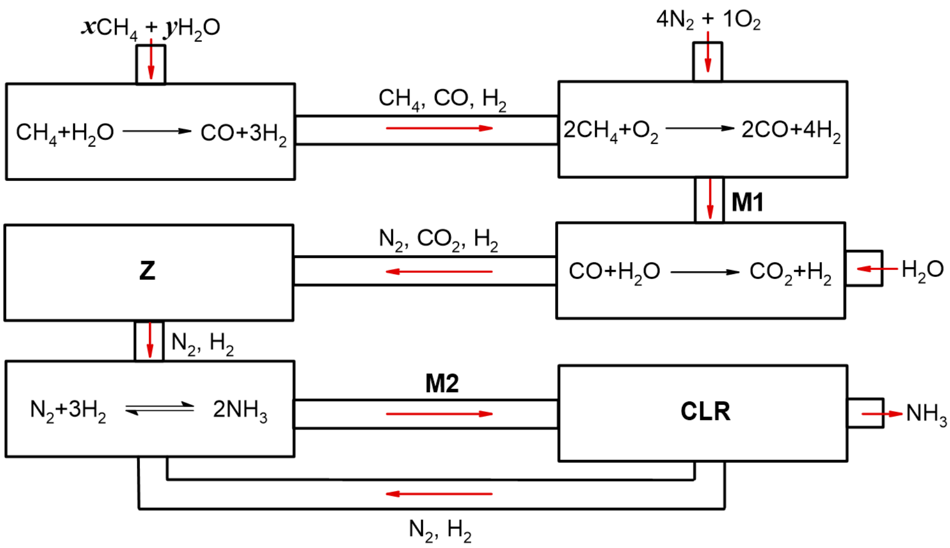


Fig. 1. **M1** - Mixture 1, **M2** - Mixture 2, **Z** – CO_2 scrubber, **CLR** - cooler

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

SOLUTION:

	CH_4	H_2O	CO	O_2	H_2	N_2	NH_3	CO_2
M1			✓		✓	✓		
M2					✓	✓	✓	

$x > y$	$x = y$	$x < y$
✓		

For composition of **M1**: 1 pt
For two correct ticks: 0.5 pt; If only one correct tick given: 0.25 pt
-0.25 pt penalty for each incorrect tick, but not below 0 pt.
For composition of **M2**: 1 pt; For two correct ticks: 0.5 pt; If only one correct tick given: 0.25 pt
-0.25 pt penalty for each incorrect tick, but not below 0 pt.
For relationship: 1 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

SOLUTION:

$n(NH_3) = \frac{6.6\cdot10^{11}}{17} = 3.88\cdot10^{10}$ mol

$n(N_2,\ \text{init.}) = \frac{3.88\cdot10^{10}}{2\cdot0.97} = 2\cdot10^{10}$ mol

$n(H_2,\ \text{init.}) = 3\cdot2\cdot10^{10} = 6\cdot10^{10}$ mol

$n(O_2) = 2\cdot10^{10}\cdot\frac{1}{4} = 5\cdot10^{9}$ mol

$$\overset{1\cdot10^{10}}{2CH_4} + \overset{5\cdot10^{9}}{O_2} \rightarrow \overset{1\cdot10^{10}}{2CO} + \overset{2\cdot10^{10}}{4H_2}$$

$$\overset{x}{CH_4} + H_2O \rightarrow \overset{x}{CO} + \overset{3x}{3H_2}$$

$$\overset{x+1\cdot10^{10}}{CO} + H_2O \rightarrow CO_2 + \overset{x+1\cdot10^{10}}{H_2}$$

$6\cdot10^{10} = 2\cdot10^{10} + 3x + x + 1\cdot10^{10}$

$x = 7.5\cdot10^{9}$

$m(CH_4) = (7.5\cdot10^{9} + 1\cdot10^{10})\cdot0.016\cdot10^{-3} = 280,000\ \text{tons}$

m(CH_4)= 280,000 tons

For $n(NH_3)$: 0.5 pt, for n $n(N_2, init.)$: 0.5 pt, for $n(H_2, init.)$: 0.5 pt, for $n(O_2, init.)$: 0.5 pt, for correct equation to calculate $n(CH_4)$: 3 pt, for $n(CH_4)$ from equation: 1 pt, for $m(CH_4)$: 2 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.

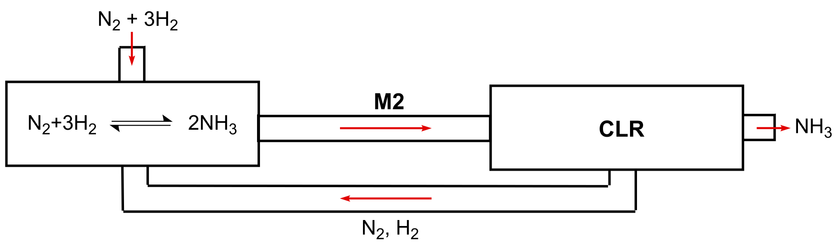


Fig. 2. **M2**. – Mixture 2, **CLR** - cooler.

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.* 15.0 pt

b) **Calculate** the number of cycles needed to increase the **overall** yield from 15.0% to 97.0%.

SOLUTION:

Each time, along with the unreacted gases, a stoichiometric mixture of N_2 and H_2 is added to the synthesis reactor. Let's define f_n as the number of moles of N_2, which are present in the reactor after the reaction and before adding the next portion. For moles of N_2, the following recurrence relation is obtained:

$f_n = (\frac{n_0}{4} + f_{n-1})(1-\eta), \quad f_1 = (1-\eta)\frac{n_0}{4}$ (**2 pt** each)

Applying the relation and using $n_0 = 4$, we obtain:

$f_2 = (1 + f_1)(1-\eta) = (1-\eta) + (1-\eta)^2$

$f_3 = (1 + f_2)(1-\eta) = (1-\eta) + (1-\eta)^2 + (1-\eta)^3$

$f_4 = (1 + f_3)(1-\eta) = (1-\eta) + (1-\eta)^2 + (1-\eta)^3 + (1-\eta)^4$

...

$f_n = (1-\eta) + (1-\eta)^2 + (1-\eta)^3 + (1-\eta)^4 + \ldots + (1-\eta)^n = \sum_{i=1}^{n}(1-\eta)^i$ (**2 pt**)

$= (1-\eta)\dfrac{1-(1-\eta)^n}{1-(1-\eta)} = \left(\dfrac{1}{\eta} - 1\right)(1-(1-\eta)^n)$ (**2 pt**)

a) After using the numerical values, we can easily calculate

$f_n = 5.6662$ (**2 pt**)

If student calculated the answer by calculating every single f_n and got the final answer correctly, full marks for the answer are given, but 0 for the equations.

For any other reasonable solution, giving the correct answer, full mark will be given.

b) Over n cycles, n moles of nitrogen have entered the system:

$1 - \eta_{final} = \dfrac{\left(\dfrac{1}{\eta} - 1\right)(1-(1-\eta)^n)}{n}$ (**3 pt**)

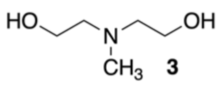
When $\eta = 0.15$ and $\eta_{final} = 0.97$, the exact answer is n = 188.9, so the required number of cycles is 189 (**2 pt**).

Note: this equation can be easily converted to a linear one by mentioning that $(1-(1-\eta)^n) \approx 1$, which is practically true after n = 30. For any other reasonable solution, giving the correct answer, full marks will be given.

n = ___189____

Total: **15 pt**

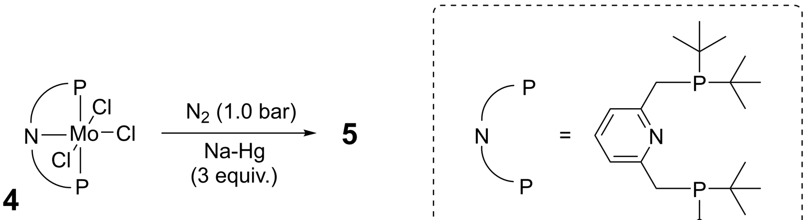
An aqueous solution of **3** is being used to remove CO_2 from the mixture.



3

7.4	**Write** the equation for this reaction. **SOLUTION:** $CO_2 + H_2O + (CH_3)N(CH_2CH_2OH)_2 \longrightarrow (CH_3)NH(CH_2CH_2OH)_2{}^+ + HCO_3{}^-$ 3 pt Any other reasonable reactions will be credited partially.	3.0 pt

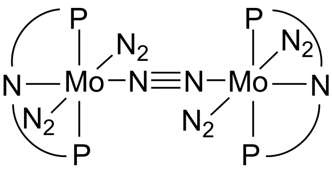
Complex **5** is obtained through the fixation of the molecular nitrogen according to the scheme below.



$M_W(\mathbf{4})$ = 597.824 g mol^{-1}

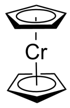
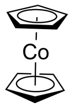
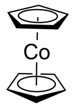
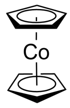
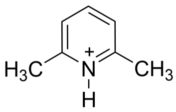
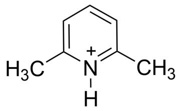
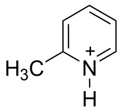
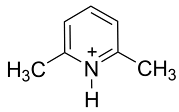
7.5 **Draw** the structure of **5** using simplified scheme for the ligand. Note that 1.00 g of **4** will react stoichiometrically with 94.97 cm^3 of N_2 at 273.15 K and 1.0 bar. — 6.0 pt

SOLUTION:

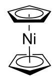
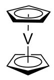
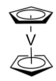
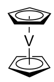
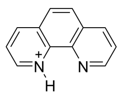
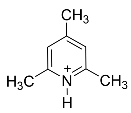
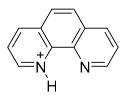
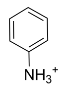
$n(N_2) = \frac{PV}{RT} = \frac{100 \times 0.09497}{8.314 \times 273.15} = 4.182 \times 10^{-3}$ mol $n(\mathbf{4}) = \frac{1.00 \text{ g}}{597.824 \text{ g mol}^{-1}} = 1.673 \times 10^{-3}$ mol $\frac{n(N_2)}{n(\mathbf{4})} = \frac{4.182 \times 10^{-3}}{1.673 \times 10^{-3}} = 2.5$ Thus, one molecule of the complex absorbs 2.5 moles of nitrogen, which means that two molecules of the complex absorb 5 molecules of nitrogen.	

For calculating the ratio of nitrogen and complex: 3 pt, for correct structure (stereochemistry is not marked): 3 pt, for any other structures, fitting the ratio: 1 pt
If student found CORRECT structure but did not show calculations, full marks will be given.

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

SOLUTION:
B>C>D>A=0
A = 0: $NiCp_2$ at −0.09 V is below the reductant threshold, so no NH_3 is produced.
B>C: B benefits from a slightly higher pK_a: stronger acids favour hydrogen evolution. It can be seen from the table as well (**3** vs **4**). (2 pt)
C>D: Switching from OTf^- to Cl^- causes a large suppression because of the stronger coordination. This is shown in the table (**2** vs **3**). (2 pt)
D>A: D gives small non-zero yield — Cl^- suppresses heavily but the strong reductant and good pK_a sustain some catalytic turnover (**2**), when **A** gives zero. (2 pt)
Total: 6 pt

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

SOLUTION:

For binary nitride Z_3N_n (we can suggest nitrogen as trivalent for the start):

$w(\mathrm{N}) = \dfrac{14.007 \times n(\mathrm{N})}{14.007 \times n(\mathrm{N}) + M(\mathrm{Z}) \times 3}$, so $M(\mathrm{Z}) = \dfrac{14.007}{3}\left(\dfrac{1}{w(\mathrm{N})} - 1\right) \times n$

For analysing mass fraction data let's create a table:

n	$M(Z_7)$	$M(Z_8)$	$M(Z_9)$
1	46.30	20.03	7.02
2	92.61	**40.07** (Ca_3N_2)	14.04
3	**138.909** (LaN)	60.105	21.063
4	185.21	80.14	28.08 (Si_3N_4)
5	231.52	100.18	35.11
6	277.82	120.21	42.13
7	324.12	140.24	49.15
8	370.42	160.28	56.19

After calculations and the use of the common chemical sense we get only 3 possibilities: **7** = LaN, **8** = Ca_3N_2, **9** = Si_3N_4. Now let's convert mass ratios to molar ones:

$n(\mathrm{LaN}) : n(\mathrm{Ca_3N_2}) : n(\mathrm{Si_3N_4}) : n(\mathrm{SiO_2})$

$$\frac{5.09}{138.91{+}14.01} : \frac{2.96}{40.07{\cdot}3{+}14.01{\cdot}2} : \frac{3.27}{28.08{\cdot}3{+}14.01{\cdot}4} : \frac{1}{28.08{+}16.00{\cdot}2} = 10 : 6 : 7 : 5$$

So, the reaction of formation of **10** looks like:

$$10\,\mathrm{LaN} + 6\,\mathrm{Ca_3N_2} + 7\,\mathrm{Si_3N_4} + 5\,\mathrm{SiO_2} \longrightarrow \ldots$$

Thus, the formula of **10** should be $La_{10}Ca_{18}Si_{26}N_{50}O_{10}$. **T** should have a tetrahedral configuration, which is really unlikely for both nitrogen and oxygen, so anion **T** should have the formula SiX_4^{n-} (X might be different). As we need to have two identical monoatomic anions, which cannot be obtained from one atom of nitrogen, **T** = SiO_3N^{5-}, **S** = O^{2-}. So, the final answer is **10** = $La_5Ca_9(O)_2(NSiO_3)[Si_{12}N_{24}]$.

for **7, 8, 9**: 3 pt each (for **9** = Li_3N 1 pt);

for **10**: 4 pt if both **S** and **T** are emphasised, 2 pt for empirical formula.