Escuela Politécnica Superior
Universidad Carlos III de Madrid

FINAL EXAM

EXAM (60%)

SURNAME...NAME...........................

1.- (1.2 points) Human body approximately contains 250 g of potassium from which 0.012 % is ^{40}K, a beta emitter with $t_{1/2} = 1.25 \cdot 10^9$ y (1.311 MeV). Answer succinctly the following questions:

a) *(0.2 points)* How changes Z and N in a beta emission process?
b) *(0.2 points)* Is it typical for nuclides with N/Z >>1 or N/Z <<1?
c) *(0.2 points)* What is activity? How is it related with the mean lifetime?
d) *(0.6 points)* Calculate the activity of ^{40}K and the absorbed dose (in Gy) for a human (80 kg) along all his life (80 y).

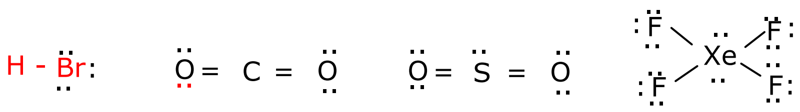
Data: 1MeV = 10^6 eV; 1 eV = $1.6 \cdot 10^{-19}$ J; 1 y = 365.25 d; $N_A = 6.022 \cdot 10^{23}$; $M_K = 39.1\ g \cdot mol^{-1}$

Solution:
a) N decreases, to N-1, Z increases to Z+1, A constant.
b) N/Z >>1
c) Activity (A): number of disintegrations per unit time = decay rate. $A=N\lambda = N/\tau$, where τ is the mean lifetime
d)
Decay constant $\lambda=0.693/ t_{1/2} = 5.544 \cdot 10^{-10}\ y^{-1}$
Amount of K atoms in the body: 250 g<>250/39.1=6.394 mol K<>$3.85 \cdot 10^{24}$ atoms K.
Amount of ^{40}K atoms in the body: $0.00012 \cdot 3.85 \cdot 10^{24} = 4.62 \cdot 10^{20}$ atoms ^{40}K.
Activity $A=N\lambda= 4.62 \cdot 10^{20} \cdot 5.544 \cdot 10^{-10} = 2.56 \cdot 10^{11}$ d/y
Amount of energy released along 80 y: $2.56 \cdot 10^{11}$ d/y·1.311 MeV·10^6 eV/MeV·80 y=$2.69 \cdot 10^{19}$ eV <>4.3 J.
Absorbed dose: 4.3 J/80 kg=0.054 Gy <> 54 mGy.

2.- *(1 point)* Consider the following molecules HBr, CO_2, SO_2, XeF_4:

a) *(0.2 point)* Write their Lewis structures.
b) *(0.2 point)* Indicate how many lone pairs has the central atom and describe the molecular geometry.
c) *(0.2 point)* Justify which of them have non zero dipolar moment.
d) *(0.2 point)* Justify which of them are water soluble.
e) *(0.2 point)* Which is the bond order for HBr? Justify the answer.

Solution:
a)



b)
HBr 3 lone pairs; linear
CO_2 no lone pairs, linear
SO_2 1 lone pair, angular
XeF_4 2 lone pairs, square planar
c) HBr, SO_2 have non zero dipolar moment because of the unsymmetrical distribution of lone pairs
d) HBr and SO_2 will be more polar so they will be more water soluble
e) H uses $1s^1$ atomic orbital and Br one $4p^1$ of its five atomic orbitals to form a molecular sigma (σ) bond. Since each atom contributes with one electron they will form a single σ bond. The σ^* antibonding molecular orbital will be empty so the bond order will be 1.

3.- *(1 point)* Concerning thermochemistry answer the following questions:

a) *(0.25 point)* What is internal energy?

Internal Energy, E, of a system is that energy that only depends on the nature of the system and is independent on its position in any force field or its rest or motion state. Therefore Internal Energy is the sum of the kinetic energy of the molecules or atoms of the system (associated to translations, rotations and vibrations) and the potential energy associated to intermolecular forces.

b) *(0.25 point)* What is enthalpy?

Is the absorbed or released heat in a constant pressure process

c) *(0.25 point)* What are reversible and irreversible processes? Explain using a gas expansion process.

In a reversible expansion process, internal and external pressures differ only infinitesimally. That means that the process is done very slowly. $P_{int}=P_{ext}+dP$ or $P_{ext}=P_{int}-dP$.

In irreversible processes internal and external pressures are different and $P_{ext} < P_{int}$.

d) *(0.25 point)* We need to compress a gas inside a piston. How we do it with as little work as possible?

In a reversible way since $w_{rev} < w_{irr}$.

4.- *(1.4 points)* A 258.3 cm^3 chamber equipped with a piston contains CH_4 at 10 atm. and 77ºC. 6.4 g of O_2 are injected in the chamber, being this amount more than needed for a complete combustion of methane. After combustion the system returns to the initial temperature and it is found 5 L of a gas mixture at an unknown pressure over a certain amount of liquid water.

a) *(0.2 points)* Balance the combustion equation.
b) *(0.8 point)* Find the amount of water in the gas mixture and the volume of liquid water.
c) *(0.4 points)*Calculate the volume percentage composition of the gas mixture after combustion.

Data: $\rho(H_2O_L, 77ºC)= 0.978\ g\cdot cm^{-3}$; $P(H_2O_g, 77ºC)= 314.1$ mmHg; $R = 0.082\ atm\cdot L\cdot mol^{-1}\cdot K^{-1}$; $M(O_2)= 32\ g\cdot mol^{-1}$; $M(H_2O)= 18\ g\cdot mol^{-1}$.

Solution:

a) $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$

b) The amount of water vapour in the gas mixture can be calculated from the water vapour pressure $n(w_g)=P(w_g)V/RT=(314.1/760)\cdot 10/0.082\cdot 350=0.072$ mol H_2O_g

After combustion methane transforms completely into CO_2 and water. The number of moles of CH_4 is $n_M = 10\cdot 0.2583/0.082\cdot 350 = 0.09$ moles of CH_4, which is the same as the number of moles of CO_2 (n_C). The number of moles of water (liquid plus vapour) will be $2\cdot n_C = 0.18$.

The amount of liquid water will be the difference between the total water and the water in gas phase $w_L=0.18-0.072=0.108$ mol H_2O_L<>$0.108\cdot 18=1.944$ g H_2O_L<>$1.944/0.978=1.988\ cm^3$ H_2O_L.

c) Oxygen: the initial amount of oxygen is 6.4 g <>6.4/32=0.2 mol O_2. Since combustion is complete, the amount of reacted oxygen is $2\cdot n_M = 2\cdot 0.09 = 0.18$ mol O_2. The amount of non reacted oxygen will be 0.2-0.18=0.02 mol O_2.

Methane: absent

Carbon dioxide: $n_C = 0.09$ mol CO_2

Water vapour = 0.072 mol H_2O_g.

Total number of moles in gas phase after combustion $n_T = 0.02+0.09+0.072=0.182$ mol

% O_2 = 0.02/0.182=10.98%

% CO_2 = 0.09/0.182=49.45%

$\% \ H_2O_g = 0.072/0.182 = 39.56\%$

5.- *(1.4 points)* Water is added to 16.4 g of sodium acetate to prepare 500 mL of solution. Calculate:

a) *(0.4 points)* pH of the solution.

b) *(0.6 points)* The weight of acetic acid that must be added to obtain a pH of 5?

c) *(0.4 point)* The weight of solid silver nitrate ($AgNO_3$) we must add to the initial sodium acetate solution to begin precipitation of silver acetate ($AgCH_3COO$).

Data: M(acetic acid)=60 g·mol^{-1}; M(sodium acetate)=82 g·mol^{-1}; K_a(acetic acid)=$1.8\cdot10^{-5}$; M($AgNO_3$) =170 g·mol^{-1}; K_s($AgCH_3COO$)= 1.94×10^{-3}.

Solution:

a) AcNa $\rightarrow$ Ac^- + Na^+

[AcNa]=(16.4g/(82g/mol))/0.5l= 0.4M

	Ac^- + H_2O $\leftrightarrow$	AcH +	OH^-
i)	0.4M	0	0
eq)	0.4-x	x	x

$K_h=K_W/K_a=10^{-14}/1.8\cdot10^{-5}=5.56\cdot10^{-10}=x^2/(0.4-x)\approx x^2/0.4$; $x=(0.4\cdot5.56\cdot10^{-10})^{1/2}=1.49\cdot10^{-5}$M;
pOH=4.826; pH=9.173

b) Buffer

pH=pK_a-log([acid]/[base]); 5= 4.74- log([AcH]/0.4); [AcH]= 0.222M
0.222(mol/L)·0.5L·60(g/mol)= 6.66 g acetic acid

c) $AgNO_3 \rightarrow Ag^+ + NO_3^-$

$Ag^+ + Ac^- \rightarrow AgAc_{(s)}$

$Ks=[Ac^-][Ag^+]=1.94\times10^{-3}$

$[Ag^+]= Ks/[Ac^-]= 1.94\times10^{-3} / 0.4 = 4.85\cdot10^{-3}$M

n(Ag^+) = $4.85\cdot10^{-3}$ M·0.5L=$2.425\cdot10^{-3}$ mol <> $2.425\cdot10^{-3}\cdot170$ = 0.412 g $AgNO_3$

6.- *(1.4 points)* Consider a cell in which the following reaction takes place:

$$5Fe^{2+}(ac) + MnO_4^-(ac) + 8H^+(ac) \leftrightarrow 5Fe^{3+}(ac) + Mn^{2+}(ac) + 4H_2O(l)$$

Platinum electrodes are introduced in both anode and cathode, a saline bridge connects the two electrodes and the electrodes are connected to a voltmeter.

a) *(0.2 points)* What is the standard potential of the cell?

b) *(0.2 points)* What reaction takes place in the anode and the cathode? What is the direction of electron movement through the external circuit? Draw a scheme of the cell.

c) *(0.4 points)* What is the equilibrium constant of the reaction at 25 ºC?

d) *(0.6 points)* What is the cell potential if [H^+] is decreased from its standard value to 10^{-4}M keeping constant the concentration of all other species?

Data: $E^0(MnO_4^-/Mn^{2+})$ = 1.512 V; $E^0(Fe^{3+}/Fe^{2+})$ = 0.771 V

Solution:

a) Fe^{2+} oxidizes into Fe^{3+} and MnO_4^- reduces to Mn^{2+}. The cell potential will be $E^0(MnO_4^-/Mn^{2+})$ - $E^0(Fe^{3+}/Fe^{2+})$ = 1.512 - 0.771 = 0.741 V.

b) Fe^{2+} oxidizes into Fe^{3+} in the anode and MnO_4^- reduces to Mn^{2+} in the cathode. Electrons are produced in the anode (Fe^{2+}/ Fe^{3+}electrode) and move to the cathode (Mn^{2+}/ MnO_4^-)

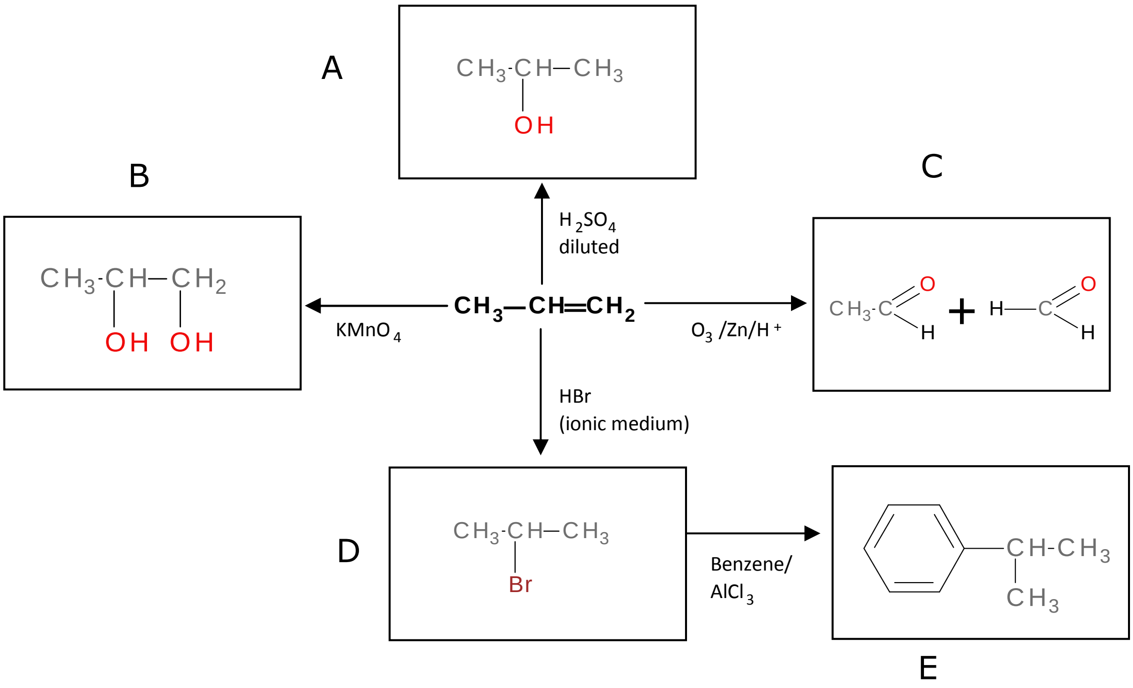
c) The equilibrium constant of the redox reaction is given by

$$E = E^0 - \frac{0.0257}{n}\ln Q = E^0 - \frac{0.059}{5}\log Q \quad at\ equilibrium\ E = 0\ and\ Q = K$$

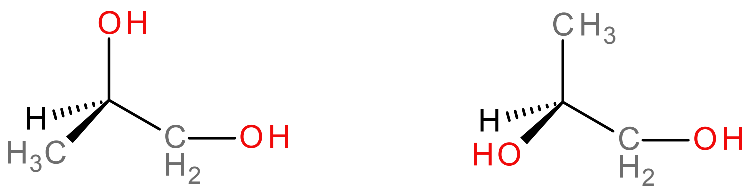
$$K = 10^{\frac{E^0 n}{0.059}} = 10^{\frac{0.739\times5}{0.059}} = 4.24\cdot10^{62}$$

d) $E = E^0 - \frac{0.059}{5}\log\frac{[Mn^{2+}]\cdot[Fe^{3+}]^5}{[MnO_4^-]\cdot[Fe^{2+}]^5\cdot[H^+]^8} = 0.739 - 0.0118\log\frac{1}{10^{-32}} = 0.361V$

7.- (*1,2 point*) Complete the following set of reactions and draw the stereoisomers of product B.



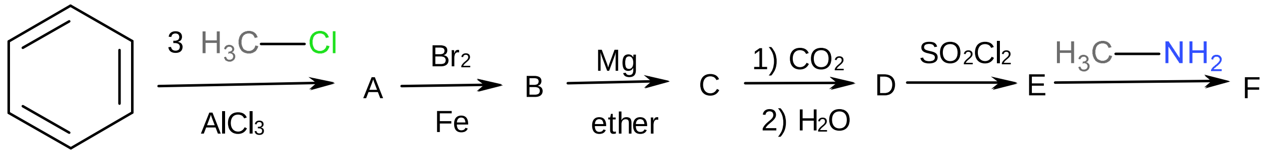
Solution: (0,2 points each correct product and 0.2 for stereoisomers)

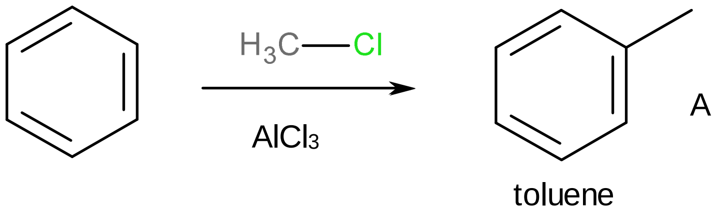


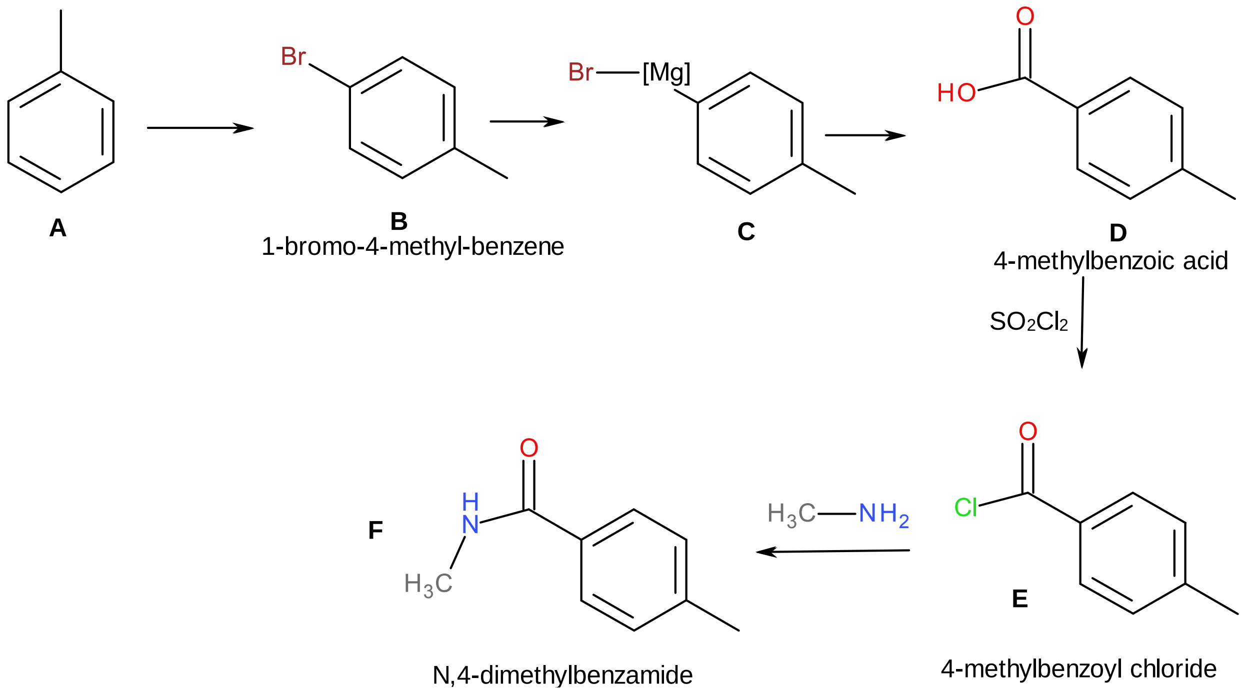
(2R)-propane-1,2-diol (2S)-propane-1,2-diol

8. (*1,4 point*) Product **A** is obtained reacting benzene with one mol of CH_3Cl using $AlCl_3$ as catalyst. **A** is subjected to the following set of reactions: a) Br_2 in the presence of iron as catalyst giving a single product **B** because of steric hindrance, b) magnesium under anhydrous conditions (ether) giving product **C**, c) carbon dioxide and subsequently water, giving the product **D**, d) thionyl chloride giving **E** which reacts with methylamine giving **F**. Deduce the structural formulas of compounds **A** to **F**.

Solution:


3 H3C—Cl
AlCl3
A
Br2
Fe
B
Mg
ether
C
1) CO2
2) H2O
D
SO2Cl2
E
H3C—NH2
F


H3C—Cl
AlCl3
A
toluene


A
Br
B
1-bromo-4-methyl-benzene
Br—[Mg]
C
HO
O
D
4-methylbenzoic acid
SO2Cl2
Cl
O
E
4-methylbenzoyl chloride
H3C—NH2
F
H
N
H3C
O
N,4-dimethylbenzamide