Theoretical problems
SOLUTIONS

PROBLEM 1

i) $[NO^+][NO_2^-]$

ii) $N_2O_3 \rightarrow NO + NO_2$

iii)
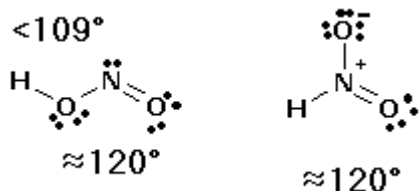
iv)
$N_2O_3 + H_2O \rightarrow 2HNO_2$

with $FeSO_4$

$NO_2^- + Fe^{2+} + 2H^+ \rightarrow NO + Fe^{3+} + H_2O$
(Or $2HNO_2 + 2FeSO_4 + H_2SO_4 \rightarrow 2NO + Fe_2(SO_4)_3 + 2H_2O$)

With acidified KI

$2NO_2^- + 2I^- + 4H^+ = 2NO + I_2 + 2H_2O$
$2Fe^{3+} + 2I^- = 2Fe^{2+} + I_2$
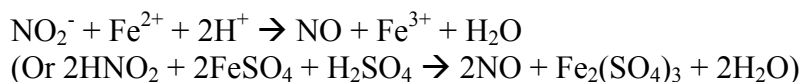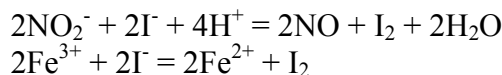
v) $2 \cdot NO \rightarrow N_2O_2$

vi)
$2NO + C \rightarrow CO_2 + N_2$
$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$
Ratio of initial concentrations is equal to ratio of moles (volume of one solution is equal to volume of another solution).
Initial amount of HNO_2 and Fe^{2+} were x mol and y mol respectively, (x-y)/2 mol of iodine was formed and x/2 mol of $CaCO_3$ precipitated:

$253,8 \cdot (x/2)=3 \cdot 100 \cdot (x-y)/2 \Rightarrow 46,2x=300y \Rightarrow$ **x:y =6,49 = 6,5**

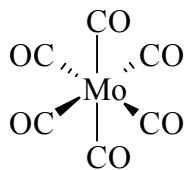vii) $2NO + Cl_2 \rightarrow 2NOCl$
$NOCl + H_2O \rightarrow HNO_2 + HCl$
$HCl \rightarrow H^+ + Cl^-$ ionizes 100%
$HNO_2 \leftrightarrow H^+ + NO_2^-$, $K_a=7,1 \cdot 10^{-4}$
$pV=nRT \Rightarrow 0,00327$ mol NO $\Rightarrow 0,00327$ mol H^+ from HCl:
$7,1 \cdot 10^{-4}=(z+0,00327)z/(0,00327-z) \Rightarrow z=5,16 \cdot 10^{-4}$, (z/0,00327)·100%=**15,8%=16%**

PROBLEM 2

1) Mo
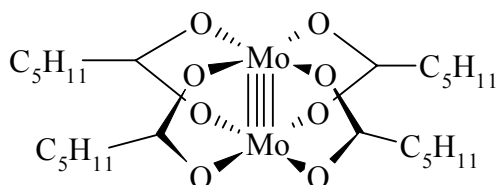
2) $Mo(CO)_6$

$$OC_{\cdots}\overset{\displaystyle CO}{\underset{\displaystyle\underset{CO}{|}}{\overset{|}{Mo}}}\overset{CO}{\underset{CO}{\diagdown}}$$
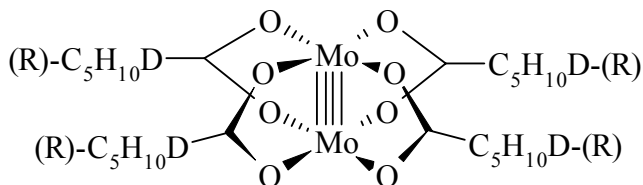
sp^3d^2

3) $Mo_2C_{24}H_{48}O_8$
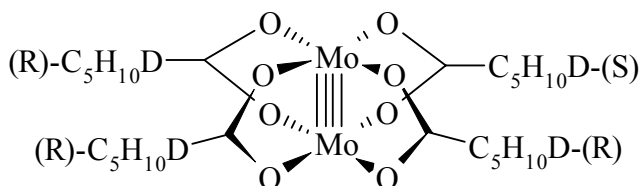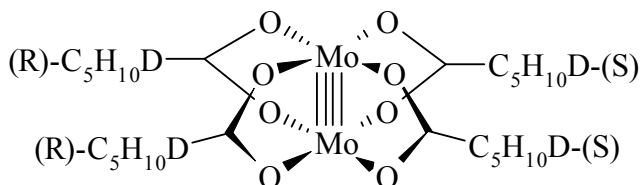
4) c)

5)

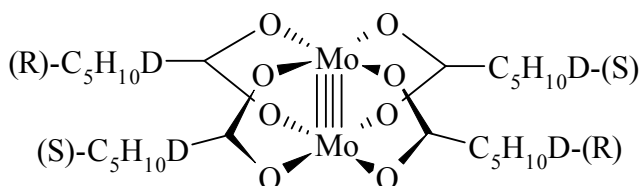Mo-O bonds are formed by dsp^2 hybrid orbitals, Mo-Mo bonds are formed by the remaining p and d orbitals.
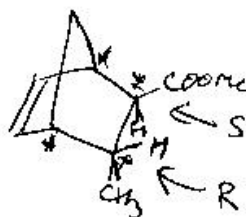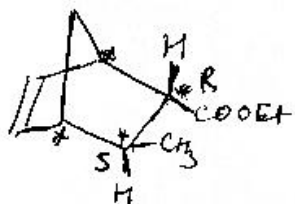

Has an enantiomer.

Has an enantiomer.

Has a plain of symmetry.

Has a center of symmetry

6) The process at the lower temperature – formation of a mesophase (liquid crystal), the process at the higher temperature – formation of an isochronous liquid. Such compounds are called liquid crystals.

PROBLEM 3

R CH₃ H *S* CH₃ COOMe H S R

H H CH₃ → Ca₃CO₂Ag

⊕ CH₂ + (cyclopentadiene)
H₂C CH₃

(cyclopentadiene) + ⊕ CH₃ →

→ ⊕ CH₃

CH₃ CH₂

H R COOEt S CH₃ H

COOMe S H R CH₃
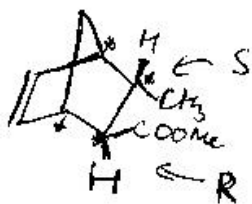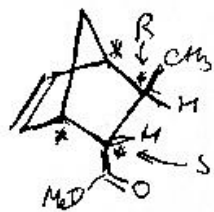
enantiomer   enantiomer

other – diastereomers

H H
ICH₂ CH₃   CH₂Cl₂, COₓCOₓ → (cyclopentadiene)

G   +   H

CH₃   CH₂

G   1. O₃ / 2. H₂O →

O OH
HO HO O O CH₃
I

t°, H⁺ →

O CH₃
HO HO O O
K

H   1. O₃ / 2. H₂O →

O
COOH COOH
Y
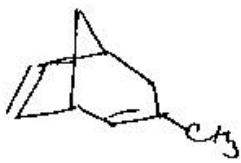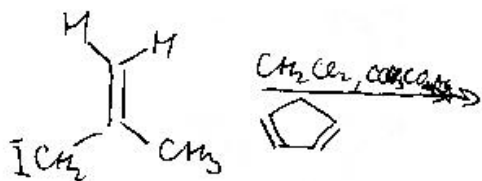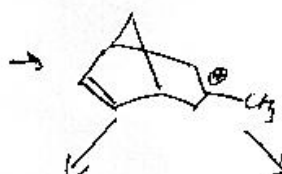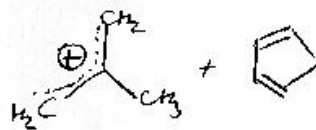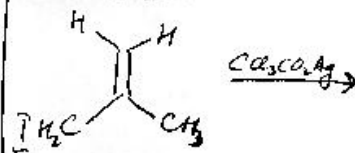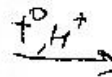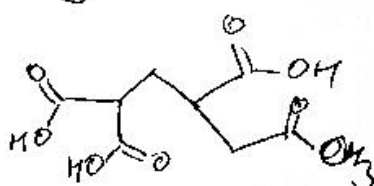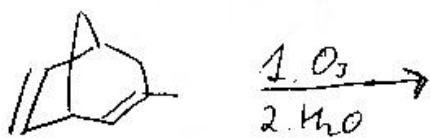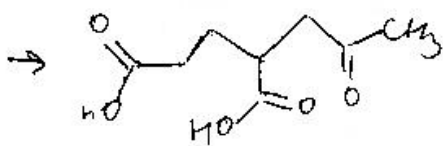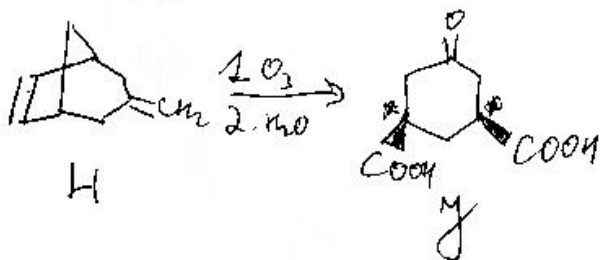
2 chiral centers
3 stereoisomers

PROBLEM 4

a) [maleic anhydride] + $C_{12}H_{25}NH_2$ ⟶ **A**

A + OH⁻ ⟶ [carboxylate] + H_2O

b), c) (Z)-**B** ⇌ (E)-**B**
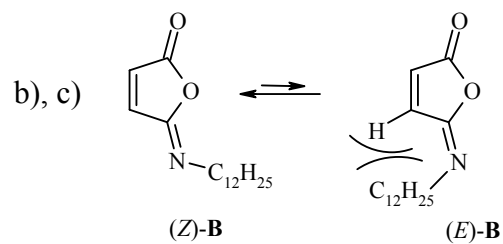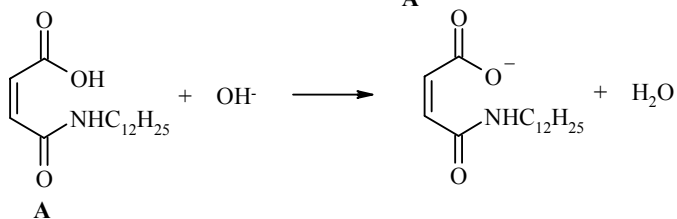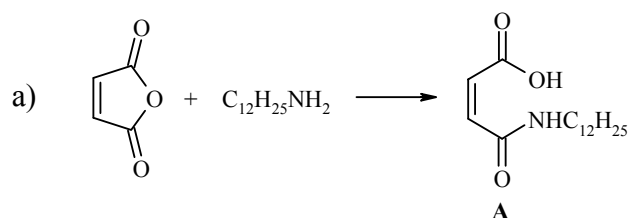
d) (Z) – signals 2, 5, 7; (E) – 1, 4, 6; (Z)+(E) – 3.

e) K_{70} = 0.134, K_{110} = 0.103 (for the equilibrium depicted in b).

$$\ln\frac{K_{110}}{K_{70}} = \frac{\Delta H}{R}\left(\frac{1}{70+273} - \frac{1}{110+273}\right), \quad \Delta H = -7180 \text{ J·mol}^{-1}.$$

f) **B** + $C_{12}H_{25}NH_2$ ⟶ **C**

g) **D**   Compound **D** has no stereoisomers

Problem 5

I.

^{63}Cu + ^{1}n → ^{64}Cu + γ; $\qquad$ ^{64}Cu → ^{64}Zn + ^{0}e$^-$ + $^0\tilde{\nu}$; $\qquad\qquad\qquad$ ^{64}Cu → ^{64}Ni + ^{0}e$^+$ + ^{0}ν.

In 25.400 h ($2T_{1/2}$) remains 25% of ^{64}Cu atoms.

%(^{64}Zn) = 75%·0.610 = **46%** $\qquad\qquad$ %(^{64}Ni) = 75%·0.390 = **29%** $\quad$ %(^{64}Cu) = **25%**

II.

^{238}U + ^{1}n → ^{239}U + γ; $\qquad\qquad$ ^{239}U → ^{239}Np + ^{0}e$^-$ + $^0\tilde{\nu}$; $\qquad\qquad$ ^{239}Np → ^{239}Pu + ^{0}e$^-$ + $^0\tilde{\nu}$.

k_1 = ln2/23.5 = 0.0295 min^{-1} = 0.000492 s^{-1}

k_2 = ln2/2.355 = 0.294 d^{-1} = 0.0123 h^{-1} = 0.000204 min^{-1} = 0.00000341 s^{-1}

if $dN\left(^{239}\text{Np}\right)/dt = 0$,

$$k_1 e^{-k_1 t_{max}} = k_2 e^{-k_2 t_{max}},$$

$$\frac{e^{-k_2 t_{max}}}{e^{-k_1 t_{max}}} = e^{k_1 - k_2 t_{max}} = \frac{k_1}{k_2} \Rightarrow t_{max} = \frac{\ln\left(\dfrac{k_1}{k_2}\right)}{k_1 - k_2},$$

$$t_{max} = \frac{\ln\left(\dfrac{k_1}{k_2}\right)}{k_1 - k_2} = \frac{\ln\left(\dfrac{0.0295}{0.000204}\right)}{0.0295 - 0.000204} = 170\ \text{min}$$

$\quad$ **i)** %(^{239}U) = 100%·e$^{-0.0295·170}$ = **0.67%**

$\quad$ **ii)** %(^{239}Np) = 100%·0.0295/(0.000204 − 0.0295)·{e$^{-0.0295·170}$ − e$^{-0.000204·170}$} = **96.60%**

$\quad$ **iii)** %(^{239}Pu) = 100% − 96.60% − 0.67% = **2.73%**

Analysis of the equation

Integration

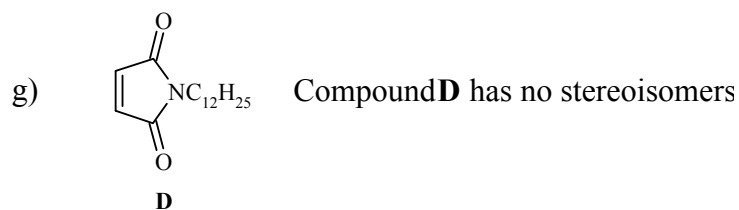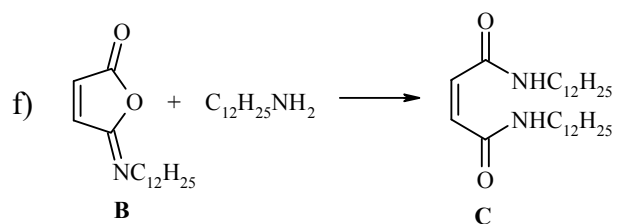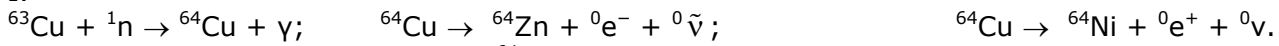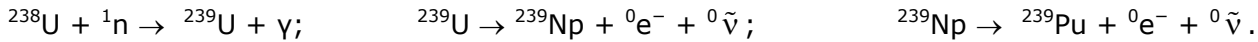$$\frac{dN\left(^{239}\text{Np}\right)}{dt} = -k_2 N\left(^{239}\text{Np}\right) + k_1 N\left(^{239}\text{U}\right)$$

239U follows a first-order rate equation, hence,

$$\frac{dN\left(^{239}\text{Np}\right)}{dt} = -k_2 N\left(^{239}\text{Np}\right) + k_1 N\left(^{239}\text{U}\right)_0 e^{-k_1 t},$$

write as

$$\frac{dN\left(^{239}\text{Np}\right)}{dt} + k_2 N\left(^{239}\text{Np}\right) = k_1 N\left(^{239}\text{U}\right)_0 e^{-k_1 t}.$$

And multiply both sides by $e^{k_2 t}$, the integrating factor

$$\left(\frac{dN\left(^{239}\text{Np}\right)}{dt} + k_2 N\left(^{239}\text{Np}\right)\right) e^{k_2 t} = k_1 N\left(^{239}\text{U}\right)_0 e^{(k_2 - k_1)t}.$$

Next notice that

$$\frac{dN\left(^{239}\text{Np}\right) e^{k_2 t}}{dt} = \left(\frac{dN\left(^{239}\text{Np}\right)}{dt} + k_2 N\left(^{239}\text{Np}\right)\right) e^{k_2 t}.$$

Hence,

$$\frac{dN\left(^{239}\text{Np}\right) e^{k_2 t}}{dt} = k_1 N\left(^{239}\text{U}\right)_0 e^{(k_2 - k_1)t},$$

which is integrated to yield

$$N\left(^{239}\text{Np}\right) e^{k_2 t} = \frac{k_1}{k_2 - k_1} N\left(^{239}\text{U}\right)_0 e^{(k_2 - k_1)t} + const,$$

Suppose $n(^{239}\text{Np})_0$ = 0 and t = 0, then we obtain: const = −(^{239}U)$_0 k_1$/($k_2 - k_1$), and the integrated equation becomes

$$N\left({}^{239}\text{Np}\right) = N\left({}^{239}\text{U}\right)_0 \frac{k_1}{k_2 - k_1}\left(e^{-k_1 t} - e^{-k_2 t}\right)$$

Laplace transformation

Linear differential equations with constant coefficients can be solved by a mathematical technigue called the Laplace transformation. Systems of zero-order or first-order reactions give rise to differential rate equations of this type, and the Laplace transformation often provides a simple solution.
Differential rate equation is

$$\frac{dN\left({}^{239}\text{U}\right)}{dt} = -k_1 N\left({}^{239}\text{U}\right),$$

taking transforms gives

$$sN\left({}^{239}\text{U}\right) - N\left({}^{239}\text{U}\right)_0 = -k_1 N\left({}^{239}\text{U}\right).$$

Solving equation for $N({}^{239}\text{U})$

$$N\left({}^{239}\text{U}\right) = \frac{N\left({}^{239}\text{U}\right)_0}{s + k_1}.$$

This is substituted into equation, which is solved for $N({}^{239}\text{Np})$
Differential rate equation is

$$\frac{dN\left({}^{239}\text{Np}\right)}{dt} = -k_2 N\left({}^{239}\text{Np}\right) + k_1 N\left({}^{239}\text{U}\right)$$

taking transforms gives

$$sN\left({}^{239}\text{Np}\right) = -k_2 N\left({}^{239}\text{Np}\right) + k_1 N\left({}^{239}\text{U}\right).$$

Substitution gives

$$N\left({}^{239}\text{Np}\right) = k_1 \frac{N\left({}^{239}\text{U}\right)_0}{\left(s + k_1\right)\left(s + k_1\right)}.$$

The inverse transformation yields

$$N\left({}^{239}\text{Np}\right) = N\left({}^{239}\text{U}\right)_0 \frac{k_1}{k_2 - k_1}\left(e^{-k_1 t} - e^{-k_2 t}\right).$$

Problem 6

Table

	Temperature T, K	Volume V, m³	Thermodynamic expansion work w, J
1. stage	273.16	0.01000	**−89.1**
2. stage	**369.81**	**18.9**	**−1.704·10⁶**
3. stage	**456.21**	10.00	**1.21·10⁶**
4. stage	456.21	5.00	**1.457·10⁶**

Calculation

$$n = \frac{10.00 \text{ dm}^3 \cdot 0.9987 \text{ g/dm}^3}{18.02 \text{ g/mol}} = 554.2 \text{ mol}$$

1. $w = -p(V_2 - V_1) = -pV_1\left(\frac{d_1}{d_2} - 1\right) = -1.000 \cdot 10^5 \text{ Pa} \cdot 10.00 \text{ dm}^3 \cdot \frac{1 \text{ m}^3}{1000 \text{ dm}^3} \cdot \left(\frac{0.9987}{0.917} - 1\right) = -89.1 \text{ J}$.

2. $\frac{1}{T_2} = \frac{R}{\Delta H} \ln \frac{p_1}{p_2} + \frac{1}{T_1} = \frac{8.3145}{40655} \ln \frac{1.01325}{0.900} + \frac{1}{273.15} = 0.0027041 \text{ K}^{-1}$,

$T_2 = 369.81 \text{ K}$.

$V_2 = \frac{nRT_2}{p_2} = \frac{554.2 \text{ mol} \cdot 8.3145 \text{ J/(mol·K)} \cdot 369.81 \text{ K}}{0.900 \cdot 10^5 \text{ Pa}} = 18.93 \text{ m}^3 \approx 18.9 \text{ m}^3$.

$w = -p(V_2 - V_1) \approx -pV_2 = -nRT = -554.2 \text{ mol} \cdot 8.3145 \text{ J/(mol·K)} \cdot 369.81 \text{ K} = -1.704 \cdot 10^6 \text{ J}$.

3. $T_3 = T_2\left(\frac{V_2}{V_1}\right)^{(\chi-1)} = 369.81 \text{ K} \cdot \left(\frac{18.93}{10.00}\right)^{(1.329-1)} = 456.21 \text{ K}$.

$w = \frac{nR(T_3 - T_2)}{\chi - 1} = \frac{554.2 \text{ mol} \cdot 8.3145 \text{ J/(K·mol)} \cdot (456.21 \text{ K} - 369.81 \text{K})}{1.329 - 1} = 1.21 \cdot 10^6 \text{ J}$.

4. $w = -nRT_3 \ln \frac{V_4}{V_3} = 554.2 \text{ mol} \cdot 8.3145 \text{ J/(mol·K)} \cdot 456.21 \text{ K} \cdot \ln\left(\frac{5.00}{10.00}\right) = 1.457 \cdot 10^6 \text{ J}$