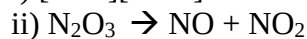


13. Baltijas valstu ķīmijas olimpiāde, 29.04.-01.05.2005. Viļņa

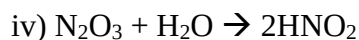
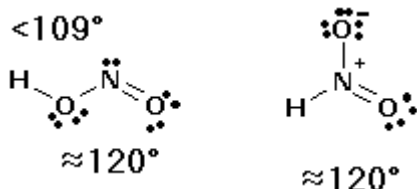
Teorētisko uzdevumu atrisinājumi.

PROBLEM 1

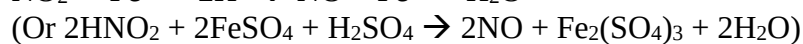
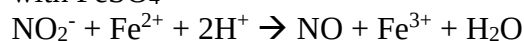
Solution



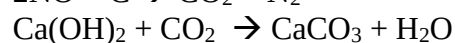
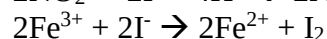
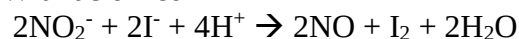
iii)



with FeSO_4



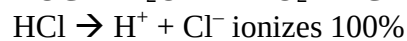
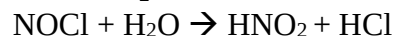
With acidified KI



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:

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

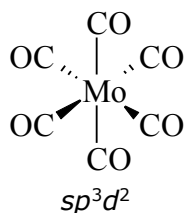


$$pV = nRT \Rightarrow 0,00327 \text{ mol NO} \Rightarrow 0,00327 \text{ mol H}^+ \text{ from HCl:}$$

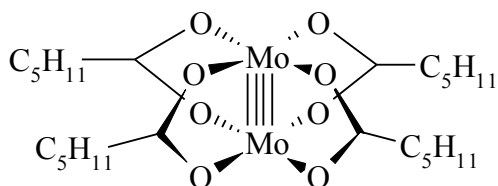
$$7,1 \cdot 10^{-4} = (z + 0,00327)z / (0,00327 - z) \Rightarrow z = 5,16 \cdot 10^{-4}, (z/0,00327) \cdot 100\% = 15,8\% = 16\%$$

PROBLEM 2**Solution**

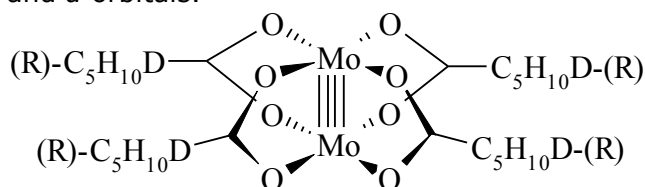
- 1) Mo
- 2) Mo(CO)₆



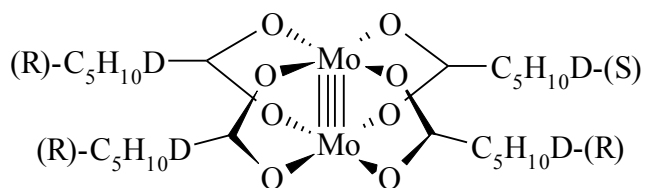
- 3) Mo₂C₂₄H₄₈O₈
- 4) c)
- 5)



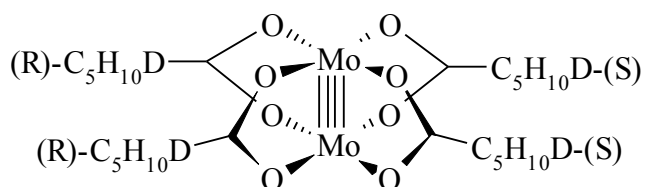
Mo-O bonds are formed by dsp^2 hybrid orbitals, Mo-Mo bonds are formed by the remaining p and d orbitals.



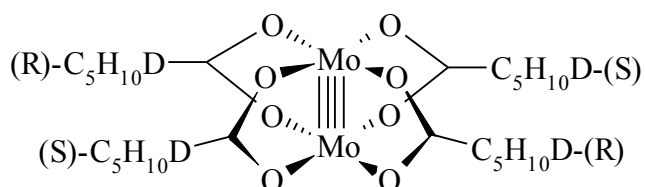
Has an enantiomer.



Has an enantiomer.



Has a plain of symmetry.

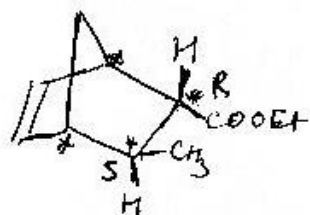
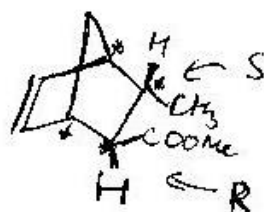
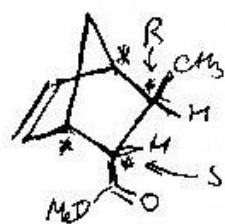


Has a center of symmetry

- 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.

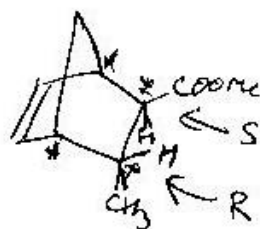
PROBLEM 3

Solution

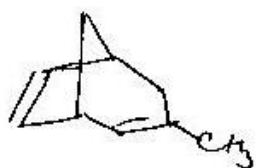
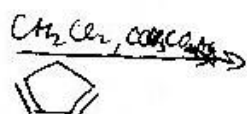
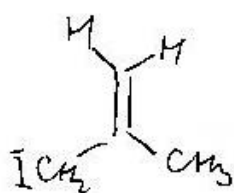


enantiomer

other - diastereomers

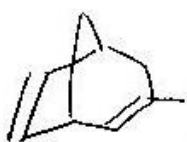
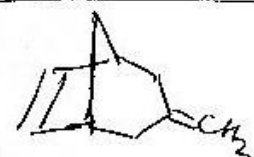


enantiomer

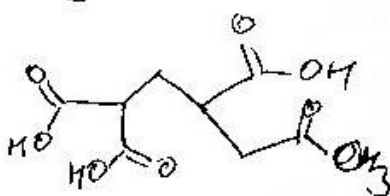
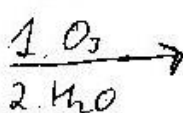


G

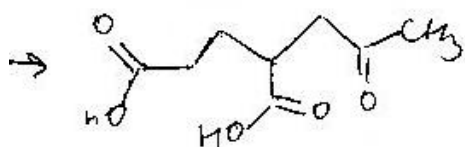
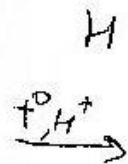
+



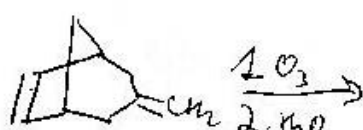
G



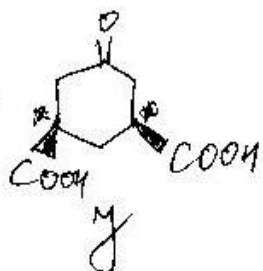
I



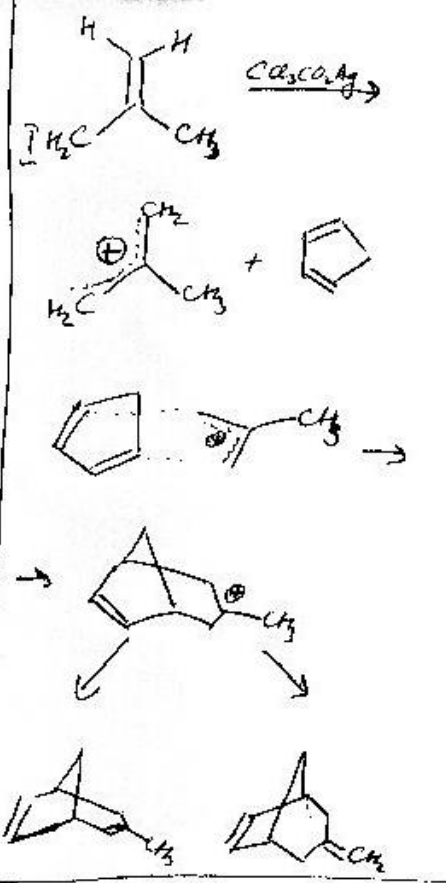
K

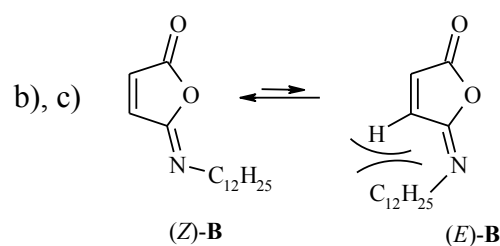
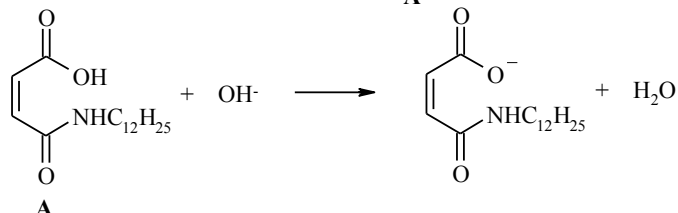
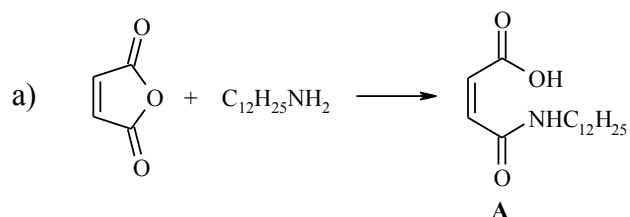


H



2 chiral centers
3 stereoisomers

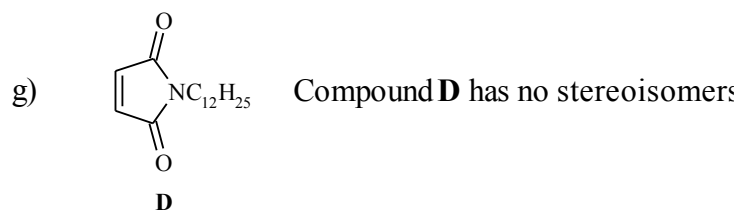
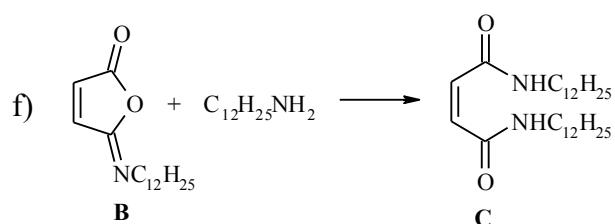


PROBLEM 4
Solution


d) (Z) – signals 2, 5, 7; (E) – 1, 4, 6; (Z)+(E) – 3.

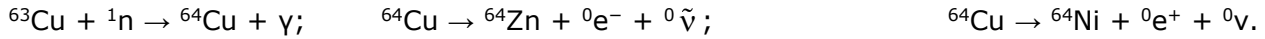
e) $K_{70} = 0.134$, $K_{110} = 0.103$ (for the equilibrium depicted in b).

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



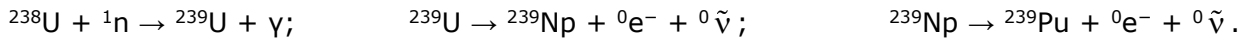
PROBLEM 5**Solution**

I.

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

$$\%(^{64}\text{Zn}) = 75\% \cdot 0.610 = \mathbf{46\%} \quad \%(^{64}\text{Ni}) = 75\% \cdot 0.390 = \mathbf{29\%} \quad \%(^{64}\text{Cu}) = \mathbf{25\%}$$

II.



$$k_1 = \ln 2 / 23.5 = 0.0295 \text{ min}^{-1} = 0.000492 \text{ s}^{-1}$$

$$k_2 = \ln 2 / 2.355 = 0.294 \text{ d}^{-1} = 0.0123 \text{ h}^{-1} = 0.000204 \text{ min}^{-1} = 0.00000341 \text{ s}^{-1}$$

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

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

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

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

$$\text{i) } \%(^{239}\text{U}) = 100\% \cdot e^{-0.0295 \cdot 170} = \mathbf{0.67\%}$$

$$\text{ii) } \%(^{239}\text{Np}) = 100\% \cdot 0.0295 / (0.000204 - 0.0295) \cdot \{e^{-0.0295 \cdot 170} - e^{-0.000204 \cdot 170}\} = \mathbf{96.60\%}$$

$$\text{iii) } \%(^{239}\text{Pu}) = 100\% - 96.60\% - 0.67\% = \mathbf{2.73\%}$$

Analysis of the equation**Integration**

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

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

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

write as

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

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

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

Next notice that

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

Hence,

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

which is integrated to yield

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

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

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

Laplace transformation

Linear differential equations with constant coefficients can be solved by a mathematical technique 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

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

taking transforms gives

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

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

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

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

Differential rate equation is

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

taking transforms gives

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

Substitution gives

$$N(^{239}\text{Np}) = k_1 \frac{N(^{239}\text{U})_0}{(s + k_1)(s + k_2)}.$$

The inverse transformation yields

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

PROBLEM 6**Solution****Table**

	Temperature T , K	Volume V , m ³	Thermodynamic expansion work w , J
1. stage	273.16	0.01000	-89.1
2. stage	369.81	18.9	-1.704·10 ⁶
3. stage	456.21	10.00	1.21·10 ⁶
4. stage	456.21	5.00	1.457·10 ⁶

Calculation

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

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

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

$$T_2 = 369.81 \text{ K}.$$

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

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

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

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

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