Baltic Chemistry Competition

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1ST ROUND, SOLUTIONS

Problem 1 (Lithuania)

Self destructing paper (6 points)

Solution

a) $$pH = pKa + \lg \frac{[\mathrm{Al(H_2O)_5(OH)}]^{2+}}{[\mathrm{Al(H_2O)_6}]^{3+}}$$

$$\frac{[\mathrm{Al(H_2O)_5(OH)}]^{2+}}{[\mathrm{Al}^{3+}]_0} = 0.529$$

$$\frac{[\mathrm{Al(H_2O)_6}]^{3+}}{[\mathrm{Al}^{3+}]_0} = 1 - 0.529 = 0.471$$

$$pKa = pH - \lg \frac{[\mathrm{Al(H_2O)_5(OH)}]^{2+}}{[\mathrm{Al(H_2O)_6}]^{3+}} = 5.00 - \lg \frac{0.529}{0.471} = 4.95$$

b)

$$\mathrm{Al_2(SO_4)_3 + 12H_2O \rightarrow 2[Al(H_2O)_6]^{3+} + 3SO_4^{2-}} \qquad [\mathrm{SO_4^{2-}}] = 3c \quad (1)$$

$$[\mathrm{Al(H_2O)_6}]^{3+} \leftrightarrow [\mathrm{Al(H_2O)_5(OH)}]^{2+} + [\mathrm{H^+}] \qquad \mathrm{K_a} = \frac{[\mathrm{Al(H_2O)_5(OH)}]^{2+}[\mathrm{H^+}]}{[\mathrm{Al(H_2O)_6}]^{3+}} \quad (2)$$

$$\mathrm{H_2O \leftrightarrow H^+ + OH^-} \qquad K_W = [\mathrm{H^+}][\mathrm{OH^-}] \quad (3)$$

$$2c = [\mathrm{Al(H_2O)_6}]^{3+} + [\mathrm{Al(H_2O)_5(OH)}]^{2+} \quad (4)$$

$$3[\mathrm{Al(H_2O)_6}]^{3+} + 2[\mathrm{Al(H_2O)_5(OH)}]^{2+} + [\mathrm{H^+}] = 2[\mathrm{SO_4^{2-}}] + [\mathrm{OH^-}] \quad (5)$$

$$\text{From (3)}: [\mathrm{OH^-}] = \frac{K_W}{[\mathrm{H^+}]} \quad (6)$$

$$\text{From (4)}: [\mathrm{Al(H_2O)_5(OH)}]^{2+} = 2c - [\mathrm{Al(H_2O)_6}]^{3+} \quad (7)$$

Using (1,6,7) in (5):

$$3[\mathrm{Al(H_2O)_6}]^{3+} + 2(2c - [\mathrm{Al(H_2O)_6}]^{3+}) + [\mathrm{H^+}] = 6c + \frac{K_W}{[\mathrm{H^+}]}$$

$$3[\mathrm{Al(H_2O)_6}]^{3+} + 4c - 2[\mathrm{Al(H_2O)_6}]^{3+} + [\mathrm{H^+}] - 6c - \frac{K_W}{[\mathrm{H^+}]} = 0$$

$$[\mathrm{H^+}] - 2c + [\mathrm{Al(H_2O)_6}]^{3+} - \frac{K_W}{[\mathrm{H^+}]} = 0 \quad (8)$$

$$\text{Using (4) in (2)}: K_a = \frac{(2c - [Al(H_2O)_6]^{3+})[H^+]}{[Al(H_2O)_6]^{3+}}$$

$$K_a[Al(H_2O)_6]^{3+} = 2c[H^+] - [H^+][Al(H_2O)_6]^{3+}$$

$$K_a[Al(H_2O)_6]^{3+} + [H^+][Al(H_2O)_6]^{3+} = 2c[H^+]$$

$$[Al(H_2O)_6]^{3+}([H^+] + K_a) = 2c[H^+]$$

$$[Al(H_2O)_6]^{3+} = \frac{2c[H^+]}{[H^+] + K_a} \qquad (9)$$

$$\text{Using (9) in (8)}: [H^+] - 2c + \frac{2c[H^+]}{[H^+] + K_a} - \frac{K_W}{[H^+]} = 0 \Big| \cdot ([H^+]^2 + K_a[H^+])$$

$$[H^+]^3 + K_a[H^+]^2 - 2c[H^+]^2 - 2cK_a[H^+] + 2c[H^+]^2 - K_W[H^+] - K_W K_a = 0$$

$$[H^+]^3 + K_a[H^+]^2 - (2cK_a + K_W)[H^+] - K_W K_a = 0$$

$$[H^+]^3 + 1.123 \cdot 10^{-5}[H^+]^2 - 5.656 \cdot 10^{-12}[H^+] - 1.123 \cdot 10^{-19} = 0$$

$[H^+] = 5.01 \cdot 10^{-7}$ M pH = 6.30

$[OH^-] = 2.00 \cdot 10^{-8}$ M

$[SO_4^{2-}] = 7.54 \cdot 10^{-7}$ M

$[Al(H_2O)_6]^{3+} = 2.15 \cdot 10^{-8}$ M

$[Al(H_2O)_5(OH)]^{2+} = 9.84 \cdot 10^{-7}$ M

Problem 2 (Latvia)

Searching for secrets of Superman (10 points)

1. Radioactive decays are 1st order reactions, so:

$$\ln \frac{C_0}{C} = kt$$

If t = t(half-life) = 250 000 years, then C = 0,5 C_0.

$$\ln 2 = k \cdot 250000$$

$$k = \frac{\ln 2}{t_{1/2}} = 2.77 \cdot 10^{-6}\, years^{-1}$$ 0.5 points

2. If C = 0,1 C_0, then:

$$\ln \frac{C_0}{0{,}1C_0} = 2.77 \cdot 10^{-6} \cdot t \quad \Rightarrow \quad t = \frac{\ln 10}{2.77 \cdot 10^{-6}} = 830482 = 8{,}3 \cdot 10^5\, years$$ 0.5 points

3. $$n_{Pu} : n_{Ta} : n_{Xe} : n_{Pm} : n_{Dialium} : n_{Hg} : n_H = \frac{15.08}{244.06} : \frac{18.06}{180.95} : \frac{27.71}{131.29} : \frac{24.02}{144.91} : \frac{10.62}{2 \cdot 26.98} : \frac{3.94}{200.59} : \frac{0.57}{1.01} =$$

$$= 0.0618 : 0.0998 : 0.211 : 0.166 : 0.197 : 0.0196 : 0.564 =$$

$$= 3.15 : 5.09 : 10.77 : 8.45 : 10.05 : 1 : 28.8 =$$

$$\approx 3 : 5 : 11 : 8.5 : 10 : 1 : 29$$

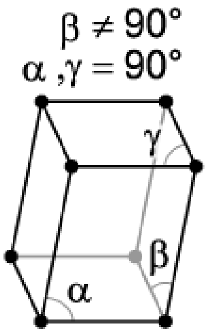
$Pu_6Ta_{10}Xe_{22}Pm_{17}(Al_2)_{20}Hg_2H_{58}$

Sum = 15.08 + 18.06 + 27.71 + 24.02 + 10.62 + 3.94 + 0.57 = 100

It is not possible mineral formula because it does not contain proper amount of anions (such as oxygen which is not in this mineral). 0.5 + 0.5 = 1 point

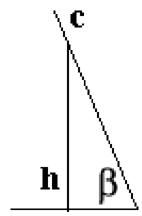
4. Fluoride ions can replace hydroxide ions in $LiNaSiB_3O_7(OH)$. Similar compounds in nature are apatite and fluoroapatite. [http://en.wikipedia.org/wiki/Apatite] 0.5 points

5. Volume of monoclinic cell is equal to area of face between **a** and **b** powers height of cell.



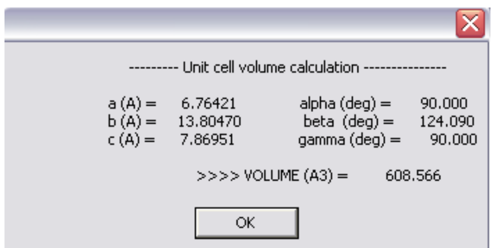
S(ab) = a * b

height = c * sin β



V = a * b * c * sin β = 6.76421 * 13.8047 * 7.86951 * sin 124.0895 = 608.566 Å^3 0.5 points

Or you can use freeware *Winplotr* to calculate cell volumes (it also works for triclinic cells) and many other data:



608.566 Å^3 = 608.566 * 10^{-30} m^3 = 608.566 * 10^{-30} * 10^6 cm^3 = 6.0856 * 10^{-22} cm^3

If we count correctly green colored lithium atoms and blue colored sodium atoms, then we can find that Z (number of molecules in unit cell) is 4.

M[$LiNaSiB_3O_7(OH)$] = 6.94 + 22.99 + 28.09 + 3 * 10.81 + 8 * 16.00 + 1.01 = 219.46 g/mol

Mass of one "molecule":

$$m_0 = \frac{M}{N_A} = \frac{219.46}{6.02 \cdot 10^{23}} = 3.6455 \cdot 10^{-22}\, g$$

$$density = \frac{m}{V} = \frac{4 \cdot m_0}{V} = \frac{4 \cdot 3.6455 \cdot 10^{-22}}{6.0856 \cdot 10^{-22}} = 2.396\, g \cdot cm^{-3}$$ 1 point

6. Bragg equation:

$$n\lambda = 2d \cdot \sin\theta,$$

where:

- *n* is an integer determined by the order given (in this problem it is 1),
- λ is the wavelength of X-rays, and moving electrons, protons and neutrons (λ = 0.15418 nm = 1.5418 Å),
- *d* is the spacing between the planes in the atomic lattice, and
- θ is the angle between the incident ray and the scattering planes.

So from this equation:

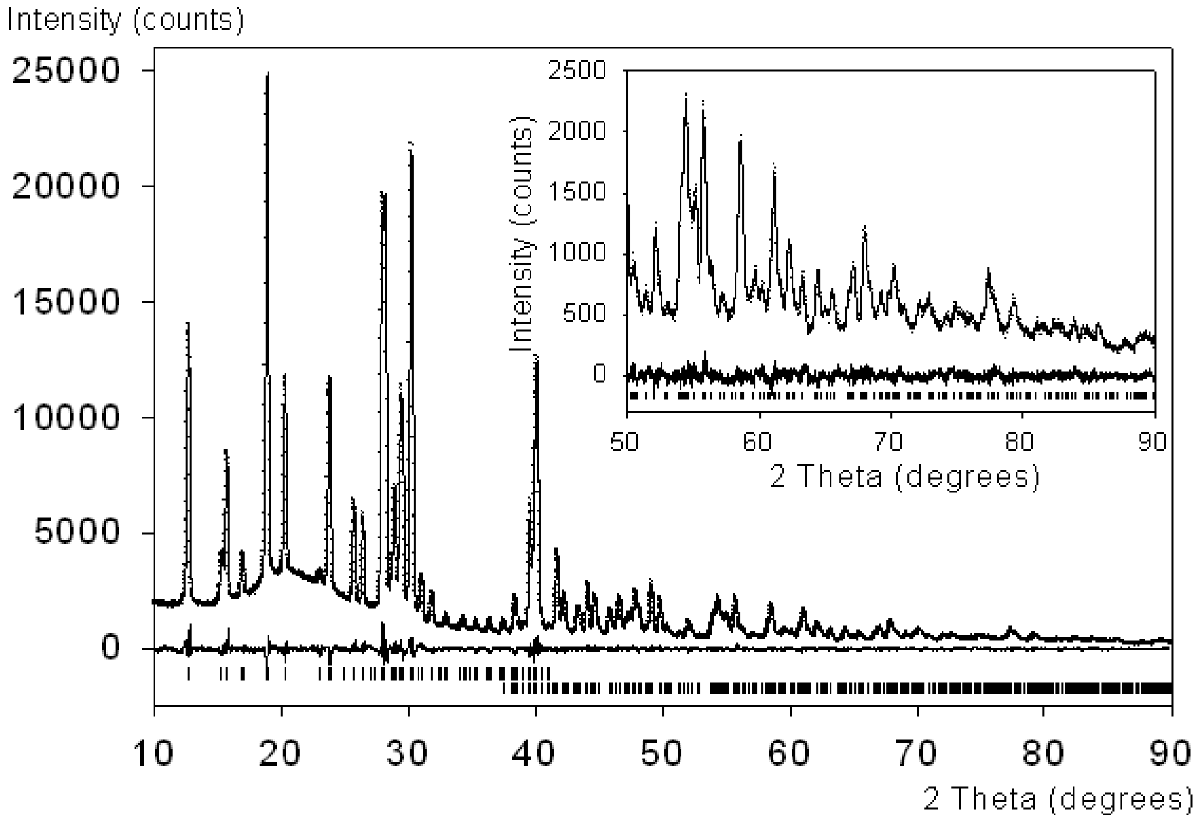
$$\sin\frac{2\theta}{2} = \frac{\lambda}{2d}$$

$$2\theta = 2 \cdot \arcsin\left(\frac{\lambda}{2d}\right)$$

d-spacing (Å)	Relative intensity	2-theta, °
4.666	62	19,02
3.716	39	23,95
3.180	82	28,06
3.152	74	28,31
3.027	40	29,51
2.946	100	30,34
2.252	38	40,04

0.5 points

Jadarite PXRD pattern (found somewhere in literature; Bruker AXS presentation, Riga, 2009) and it corresponds to results calculated. In all calculated positions we can find diffraction signals.



7. None of those diffraction patterns refers to jadarite. (0.5 points)
8. $^{238}_{92}U \rightarrow ^{234}_{90}Th + ^{4}_{2}He$ α decay

   $^{234}_{90}Th \rightarrow ^{234}_{91}Pa + ^{0}_{-1}e$ β decay

   $^{234}_{91}Pa \rightarrow ^{234}_{92}U + ^{0}_{-1}e$ β decay

   $^{234}_{92}U \rightarrow ^{230}_{90}Th + ^{4}_{2}He$ α decay

   $^{230}_{90}Th \rightarrow ^{226}_{88}Ra + ^{4}_{2}He$ α decay

   $^{226}_{88}Ra \rightarrow ^{222}_{86}Rn + ^{4}_{2}He$ α decay 0.5 points
9. Firstly we have to calculate amount of water in given hydrate. $Cu(UO_2)_2(PO_4)_2 \cdot (8\text{-}12)H_2O$

$$w(H_2O) = 0.206 = \frac{M(H_2O)\cdot x}{M(anhydrous\ compound) + M(H_2O)}$$

$$18x = 0.206\cdot(793.55 + 18x)$$

Molar mass calculations:

M_r	n	M_r * n
63.55	1	63.55
238.03	2	476.06
16	12	192
30.97	2	61.94
	sum	793.55

$$18x = 163.47 + 3.708x$$

$$14.292x = 163.47$$

$$x = 11.4$$

So molar mass of hydrated compound $Cu(UO_2)_2(PO_4)_2\cdot(11.4)H_2O$ is:

M = 793.55 + 11.4 * 18 = 999 g/mol

n[$Cu(UO_2)_2(PO_4)_2\cdot(11.4)H_2O$] = $\frac{m}{M} = \frac{5.00}{999.4} = 0.005003$ mol ≈ 0.005 mol

$N_0 = N_A$ * n = 6.02 * 10^{23} * 0.005 *** 2**= **6.0 * 10^{21} atoms** (corrected later) 1 point

10. Formation of 234-Th and 234-Pa can be assigned as negligible and it can be assumed that 238-U decays to form 234-U with half life of 4.468 * 10^9 years.

$$\frac{\Delta N(^{238}U)}{\Delta t} \approx \frac{dN(^{238}U)}{dt} = -k_0 \cdot N_{238U}$$

$$\frac{\Delta N(^{234}U)}{\Delta t} \approx \frac{d(^{234}U)}{dt} = k_0 \cdot N_{238U} - k_1 \cdot N_{234U}$$

$$\frac{\Delta N(^{230}Th)}{\Delta t} \approx \frac{d(^{230}Th)}{dt} = k_1 \cdot N_{234U} - k_2 \cdot N_{230Th}$$

$$\frac{\Delta N(^{226}Ra)}{\Delta t} \approx \frac{d(^{226}Ra)}{dt} = k_2 \cdot N_{230Th} - k_3 \cdot N_{226Ra}$$

$$\frac{\Delta N(^{222}Rn)}{\Delta t} \approx \frac{d(^{222}Rn)}{dt} = k_3 \cdot N_{226Ra}$$

At the beginning: $N_0(^{238}U)$ = 0.992742 * 3.0 * 10^{21} = 2.99 * 10^{21} atoms

$N_0(^{234}U)$ = 0.000054 * 3.0 * 10^{21} = 1.63 * 10^{17} atoms

$N_0(^{230}Th) = 0$

$N_0(^{226}Ra) = 0$

$N_0(^{222}Rn) = 0$

$$k_0 = \frac{\ln 2}{4.468 \cdot 10^9} = 1.55 \cdot 10^{-11}\, years^{-1}$$

$$k_1 = \frac{\ln 2}{245500} = 2.82 \cdot 10^{-6}\, years^{-1}$$

$$k_2 = \frac{\ln 2}{75380} = 9.19 \cdot 10^{-6}\, years^{-1}$$

$$k_3 = \frac{\ln 2}{1602} = 0.0004327 \cdot 10^{-6}\, years^{-1}$$

$$\Delta N(^{238}U) = -k_0 \cdot N_{238U} \cdot \Delta t$$

where Δt is as small as possible.

$$N(^{238}U)_{at\ t+\Delta t} = N(^{238}U)_{at\ t} + \Delta N(^{238}U)$$

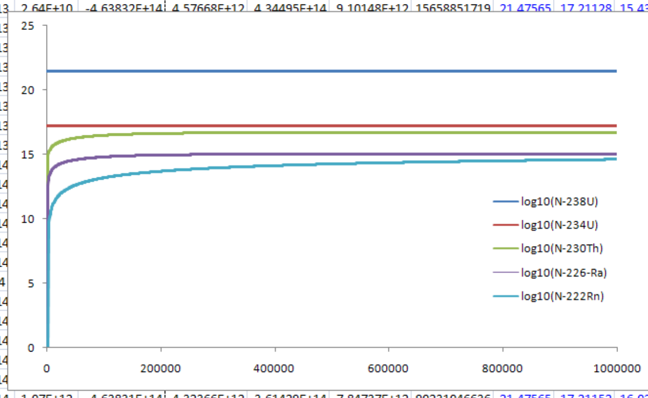
for rest particles similar equations can be obtained. 1 point

Inputting them into *MS Excel* worksheet we can obtain results that are shown below. *MS Excel* function =max(..) is used to find maximum value of 230-Th in 1 million years. It has been found that after one million years it is 5.03895 * 10^{16} atoms (maximum value for that time) and value of 5.04274*10^{16} years can be achieved in 1.974 million years.

Correct: 1.00855*10^{17} atoms in 1.974 million years.

G2 =MAX(D5:D1005)

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P
1	k0	k1	k2	k3	Δt	maxiumm value in 1 million years			maximum value of 230Th in 5 million years							
2	1,55136E-10	2,82E-06	9,2E-06	0,000432676	1000		5,03895E+16			5,04274E+16						
3												Calculate logarithms of N (to have better graph)				
4	time, years	N(238-U)	N(234-U)	N(230-Th)	N(226-Ra)	N(222-Rn)	dN(238-U)	dN(234-U)	dN(230-Th)	dN(226-Ra)	dN(222-Rn)	238U	234U	230Th	226Ra	222Rn
5	0	2,99E+21	1,63E+17	0	0	0	-4,63833E+14	4,65542E+12	4,59177E+14	0	0	21,47565	17,21121	0	0	0
6	1000	2,99E+21	1,63E+17	4,59177E+14	0	0	-4,63833E+14	4,6422E+12	4,54968E+14	4,22231E+12	0	21,47565	17,21122	14,66198	0	0
7	2000	2,99E+21	1,63E+17	9,14145E+14	4,22E+12	0	-4,63833E+14	4,62902E+12	4,50798E+14	6,57902E+12	1826891283	21,47565	17,21123	14,961015	12,62555	0
8	3000	2,99E+21	1,63E+17	1,36494E+15	1,08E+13	1,83E+09	-4,63833E+14	4,61588E+12	4,46665E+14	7,87769E+12	4673474926	21,47565	17,21124	15,135115	13,033477	9,2617127
9	4000	2,99E+21	1,63E+17	1,81161E+15	1,87E+13	6,5E+09	-4,63832E+14	4,60278E+12	4,42571E+14	8,57645E+12	8081961565	21,47565	17,21126	15,258064	13,271354	9,8129378
10	5000	2,99E+21	1,63E+17	2,25418E+15	2,73E+13	1,46E+10	-4,63832E+14	4,58971E+12	4,38515E+14	8,93523E+12	11792788800	21,47565	17,21127	15,352989	13,435454	10,163827
11	6000	2,99E+21	1,63E+17	2,69269E+15	3,62E+13	2,64E+10	-4,63832E+14	4,57668E+12	4,34495E+14	9,10148E+12	15658851719	21,47565	17,21128	15,430187	13,558597	10,421194
12	7000	2,99E+21	1,63E+17	3,12719E+15	4,53E+13									154	13,656023	10,6236
13	8000	2,99E+21	1,63E+17	3,5577E+15	5,45E+13									117	13,736006	10,789798
14	9000	2,99E+21	1,63E+17	3,98427E+15	6,36E+13									349	13,803496	10,930391
15	10000	2,99E+21	1,63E+17	4,40693E+15	7,27E+13									136	13,861665	11,051967
16	11000	2,99E+21	1,63E+17	4,82571E+15	8,18E+13									561	13,912648	11,158894
17	12000	2,99E+21	1,63E+17	5,24066E+15	9,08E+13									386	13,957943	11,254211
18	13000	2,99E+21	1,63E+17	5,6518E+15	9,97E+13									187	13,998633	11,340116
19	14000	2,99E+21	1,63E+17	6,05917E+15	1,09E+14									413	14,035528	11,418245
20	15000	2,99E+21	1,63E+17	6,46282E+15	1,17E+14									422	14,069242	11,489849
21	16000	2,99E+21	1,63E+17	6,86276E+15	1,26E+14									499	14,100255	11,555903
22	17000	2,99E+21	1,63E+17	7,25904E+15	1,35E+14									879	14,128946	11,61718
23	18000	2,99E+21	1,63E+17	7,65168E+15	1,43E+14									757	14,155621	11,674307
24	19000	2,99E+21	1,63E+17	8,04073E+15	1,52E+14									296	14,180529	11,727793
25	20000	2,99E+21	1,63E+17	8,42621E+15	1,6E+14									632	14,203876	11,778063
26	21000	2,99E+21	1,63E+17	8,80816E+15	1,68E+14									885	14,225834	11,82547
27	22000	2,99E+21	1,63E+17	9,18662E+15	1,76E+14									156	14,246548	11,870313
28	23000	2,99E+21	1,63E+17	9,5616E+15	1,85E+14									531	14,266141	11,912847
29	24000	2,99E+21	1,63E+17	9,93315E+15	1,93E+14									087	14,284721	11,953292
30	25000	2,99E+21	1,63E+17	1,03013E+16	2,01E+14									892	14,302378	11,991837
31	26000	2,99E+21	1,63E+17	1,06661E+16	2,09E+14	1,07E+12	-4,63831E+14	4,32366E+12	3,61429E+14	7,84737E+12	90231046636	21,47565	17,21152	16,028004	14,319193	12,028646
32	27000	2,99E+21	1,63E+17	1,10275E+16	2,16E+14	1,16E+12	-4,63831E+14	4,31138E+12	3,58118E+14	7,77547E+12	93626415668	21,47565	17,21153	16,042477	14,335235	12,063864



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1972	1967000	2,99E+21	1,64E+17	5,04274E+16	1,07E+15	8,59E+14	-4,63691E+14	-7490807316	153108528,5	4369216,688	4,63699E+11
1973	1968000	2,99E+21	1,64E+17	5,04274E+16	1,07E+15	8,6E+14	-4,63691E+14	-7541592846	130551017,4	3886650,75	4,63699E+11
1974	1969000	2,99E+21	1,64E+17	5,04274E+16	1,07E+15	8,6E+14	-4,63691E+14	-7592234978	108057542,9	3405455	4,63699E+11
1975	1970000	2,99E+21	1,64E+17	5,04274E+16	1,07E+15	8,61E+14	-4,63691E+14	-7642734115	85627920,5	2925625,188	4,63699E+11
1976	1971000	2,99E+21	1,64E+17	5,04274E+16	1,07E+15	8,61E+14	-4,63691E+14	-7693090660	63261967,19	2447157,563	4,63699E+11
1977	1972000	2,99E+21	1,64E+17	5,04274E+16	1,07E+15	8,61E+14	-4,63691E+14	-7743305018	40959499,94	1970048,313	4,63699E+11
1978	1973000	2,99E+21	1,64E+17	5,04274E+16	1,07E+15	8,62E+14	-4,63691E+14	-7793377588	18720336,5	1494293,25	4,63699E+11
1979	1974000	2,99E+21	1,64E+17	**5,04274E+16**	1,07E+15	8,62E+14	-4,63691E+14	-7843308772	-3455705,06	1019888,625	4,63699E+11
1980	1975000	2,99E+21	1,64E+17	5,04274E+16	1,07E+15	8,63E+14	-4,63691E+14	-7893098969	-25568805,8	546830,625	4,63699E+11
1981	1976000	2,99E+21	1,64E+17	5,04274E+16	1,07E+15	8,63E+14	-4,63691E+14	-7942748576	-47619146,4	75115,375	4,63699E+11
1982	1977000	2,99E+21	1,64E+17	5,04274E+16	1,07E+15	8,64E+14	-4,6369E+14	-7992257991	-69606907,3	-395261	4,63699E+11
1983	1978000	2,99E+21	1,64E+17	5,04274E+16	1,07E+15	8,64E+14	-4,6369E+14	-8041627609	-91532267,8	-864302,438	4,63699E+11
1984	1979000	2,99E+21	1,64E+17	5,04274E+16	1,07E+15	8,65E+14	-4,6369E+14	-8090857826	-113395407	-1332012,63	4,63699E+11
1985	1980000	2,99E+21	1,64E+17	5,04274E+16	1,07E+15	8,65E+14	-4,6369E+14	-8139949034	-135196504	-1798395,56	4,63699E+11
1986	1981000	2,99E+21	1,64E+17	5,04274E+16	1,07E+15	8,66E+14	-4,6369E+14	-8188901627	-156935736	-2263454,94	4,63699E+11

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4997	4992000	2,99E+21	1,64E+17	5,04065E+16	1,07E+15	2,26E+15	-4,63474E+14	-2,5464E+10	-7818326107	-166157425	4,63507E+11
4998	4993000	2,99E+21	1,64E+17	5,04065E+16	1,07E+15	2,26E+15	-4,63474E+14	-2,5464E+10	-7818329237	-166157493	4,63507E+11
4999	4994000	2,99E+21	1,64E+17	5,04065E+16	1,07E+15	2,26E+15	-4,63474E+14	-2,5464E+10	-7818332355	-166157559	4,63507E+11
5000	4995000	2,99E+21	1,64E+17	5,04065E+16	1,07E+15	2,26E+15	-4,63473E+14	-2,5464E+10	-7818335460	-166157626	4,63507E+11
5001	4996000	2,99E+21	1,64E+17	5,04065E+16	1,07E+15	2,26E+15	-4,63473E+14	-2,5464E+10	-7818338554	-166157692	4,63507E+11
5002	4997000	2,99E+21	1,64E+17	5,04065E+16	1,07E+15	2,26E+15	-4,63473E+14	-2,5464E+10	-7818341635	-166157759	4,63507E+11
5003	4998000	2,99E+21	1,64E+17	5,04065E+16	1,07E+15	2,26E+15	-4,63473E+14	-2,5464E+10	-7818344704	-166157824	4,63507E+11
5004	4999000	2,99E+21	1,64E+17	5,04065E+16	1,07E+15	2,26E+15	-4,63473E+14	-2,5464E+10	-7818347761	-166157890	4,63507E+11
5005	5000000	2,99E+21	1,64E+17	5,04065E+16	1,07E+15	2,27E+15	-4,63473E+14	-2,5464E+10	-7818350806	-166157955	4,63507E+11
5006											

11. See answer between graph. 0.5 points
12. Function extremes such as maximum points can be determined from function derivative. It must be equal to zero.

$$N(^{230}U)_o \frac{k_1}{k_2 - k_1}(-k_1 \cdot e^{-k_1 t} + k_2 \cdot e^{-k_2 t}) = 0$$

$$N(^{230}U)_o \frac{k_1}{k_2 - k_1} \neq 0$$

so

$$-k_1 \cdot e^{-k_1 t} + k_2 \cdot e^{-k_2 t} = 0$$

$$k_1 \cdot e^{-k_1 t} = k_2 \cdot e^{-k_2 t} \qquad \Rightarrow \qquad \frac{k_1 \cdot e^{-k_1 t}}{k_2 \cdot e^{-k_2 t}} = 1$$

$$\frac{k_1}{k_2} \cdot e^{t \cdot (k_2 - k_1)} = 1 \qquad \frac{2.82 \cdot 10^{-6}}{9.19 \cdot 10^{-6}} \cdot e^{t \cdot (9.19 \cdot 10^{-6} - 2.82 \cdot 10^{-6})} = 1$$

$$0.3069 \cdot e^{t \cdot (6.37 \cdot 10^{-6})} = 1$$

$$e^{t \cdot (6.37 \cdot 10^{-6})} = \frac{1}{0.3069} = 3.26$$

$$\ln e^{t \cdot (6.37 \cdot 10^{-6})} = \ln 3.26$$

$$t \cdot (6.37 \cdot 10^{-6}) = 1.18$$

$$t = \frac{1.18}{6.37 \cdot 10^{-6}} = 185459 \textit{ years}$$

1.5 points

13. This big difference can be explained by fact that in calculation of t_{max2} formation of ^{234}U (from ^{238}U) has not taken into account, but in Excel file it is included. If we exclude this from Excel file (simply set constant $k_0 = 0$), then we obtain same result, see figure bellow.

186	181000	2,99E+21	9,75E+16	2,96594E+16	6,3E+14	3,49E+13	0	-2,7525E+14	2,5202E+12	93979944307	2,72635E+11	21,47565	16,98895	16,472162	14,799418	13,542259
187	182000	2,99E+21	9,72E+16	2,96619E+16	6,3E+14	3,51E+13	0	-2,7447E+14	1,71988E+12	76491230004	2,72676E+11	21,47565	16,98772	16,472199	14,799483	13,545643
188	183000	2,99E+21	9,69E+16	2,96636E+16	6,3E+14	3,54E+13	0	-2,737E+14	9,29122E+11	59210268820	2,72709E+11	21,47565	16,9865	16,472224	14,799536	13,549001
189	184000	2,99E+21	9,67E+16	2,96645E+16	6,3E+14	3,57E+13	0	-2,7292E+14	1,47819E+11	42135017863	2,72734E+11	21,47565	16,98527	16,472237	14,799577	13,552334
190	185000	2,99E+21	9,64E+16	2,96647E+16	6,3E+14	3,59E+13	0	-2,7215E+14	-6,2412E+11	25263453401	2,72753E+11	21,47565	16,98404	16,47224	14,799606	13,555642
191	186000	2,99E+21	9,61E+16	2,96641E+16	6,3E+14	3,62E+13	0	-2,7139E+14	-1,3868E+12	8593570682	2,72763E+11	21,47565	16,98281	16,472231	14,799623	13,558925
192	187000	2,99E+21	9,58E+16	2,96627E+16	6,3E+14	3,65E+13	0	-2,7062E+14	-2,1403E+12	-7876616238	2,72767E+11	21,47565	16,98158	16,47221	14,799629	13,562183
193	188000	2,99E+21	9,56E+16	2,96605E+16	6,3E+14	3,68E+13	0	-2,6985E+14	-2,8846E+12	-2,4149E+10	2,72764E+11	21,47565	16,98036	16,472179	14,799624	13,565418

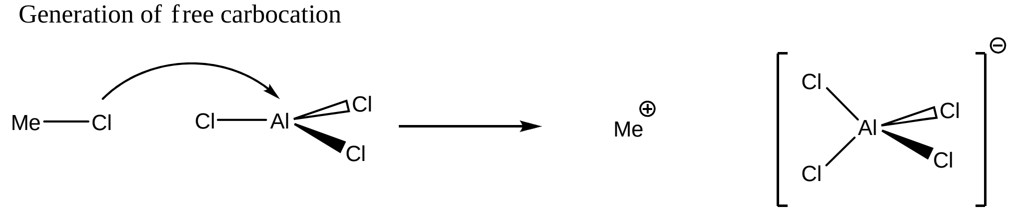
0.5 points

Problem 3 (Lithuania)

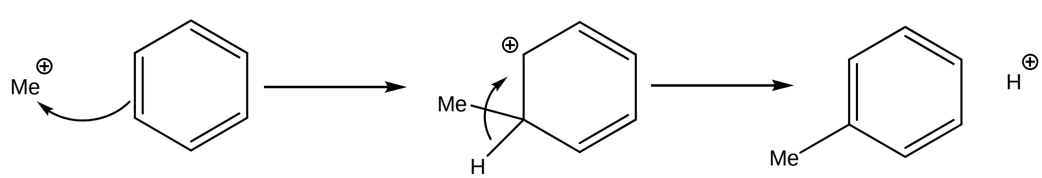
Push those arrows (8 points)

1.

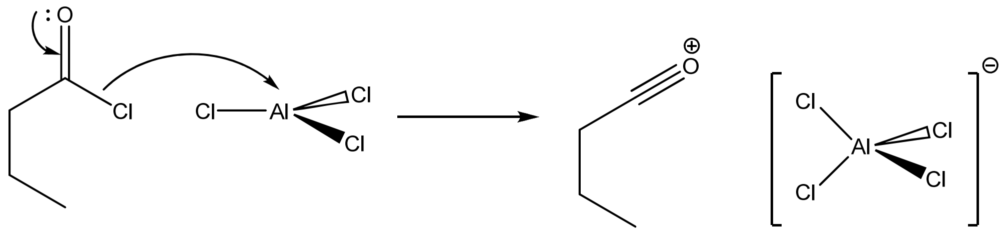
Generation of free carbocation



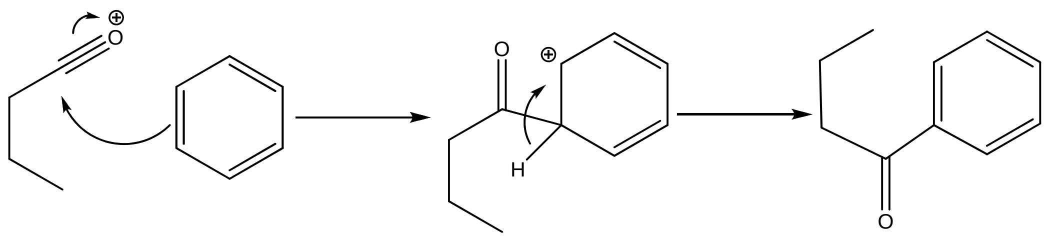
Alkylation



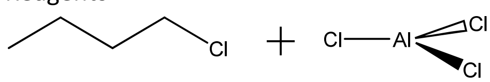
2. Generation of free carbocation



Acylation

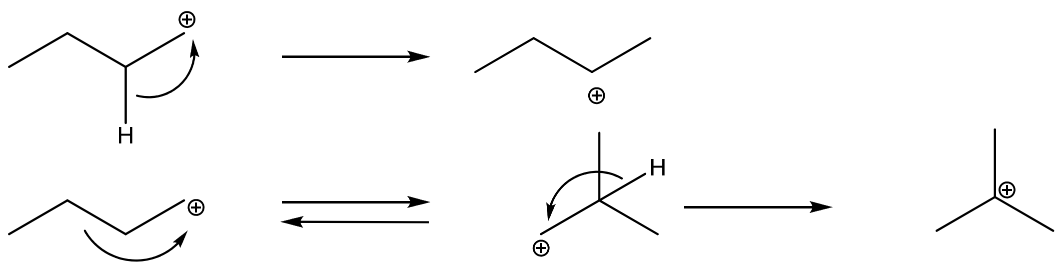


3. Reagents



Mechanism of alkylation as in part 1.

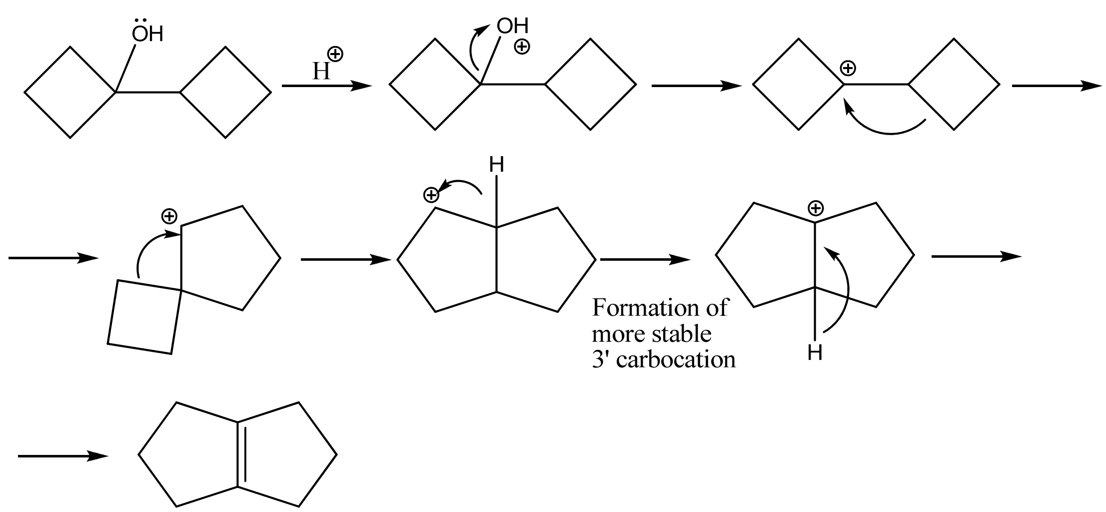
Side carbocation formation:



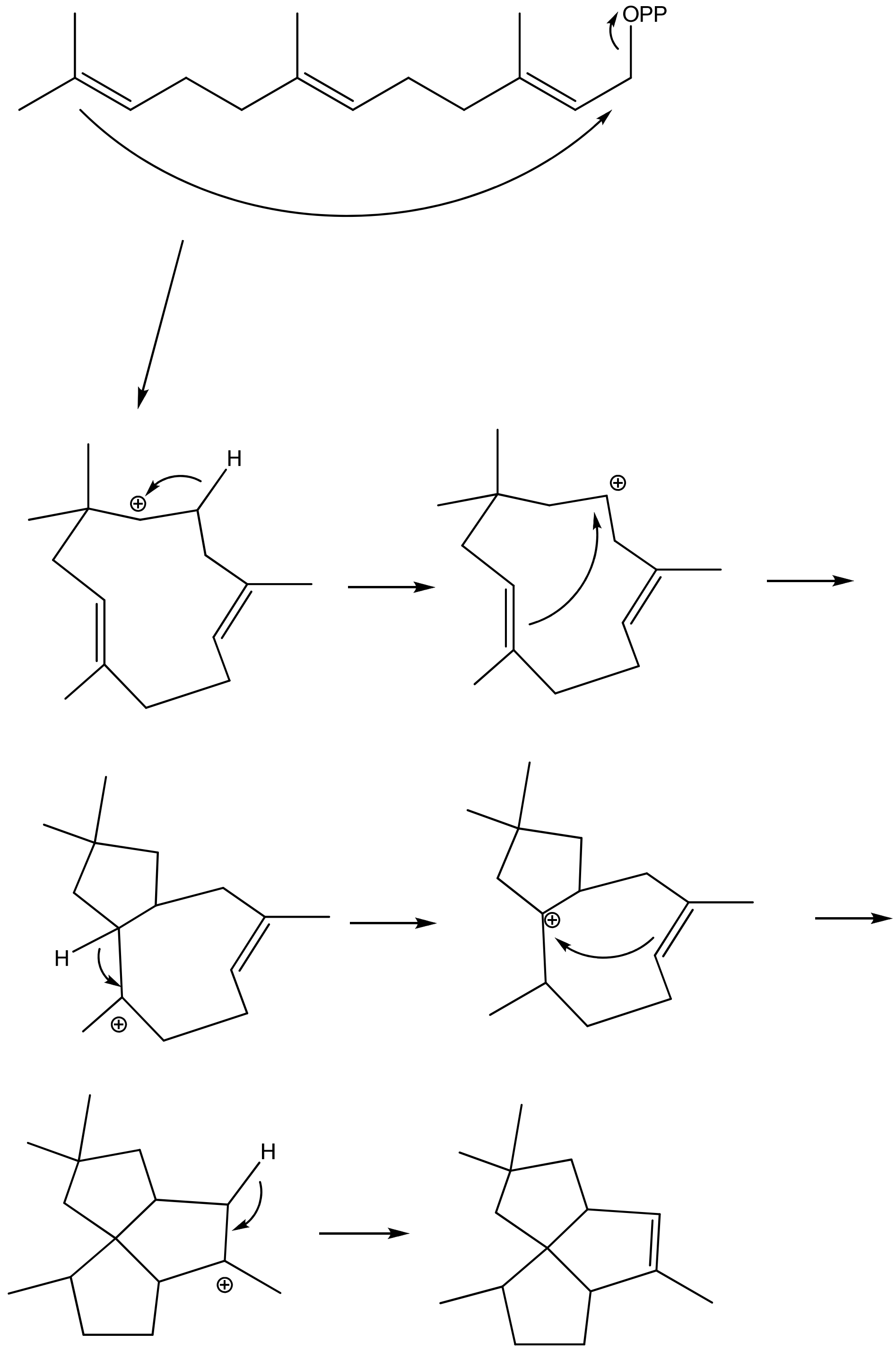
These carbocations are able to further react with the bezene thus producing side products.

Please note, that there was an error in this question. Those students, who provided even slightly logical solutions, where awarded with marks. We are sorry for the inconvenience.

4.



5.

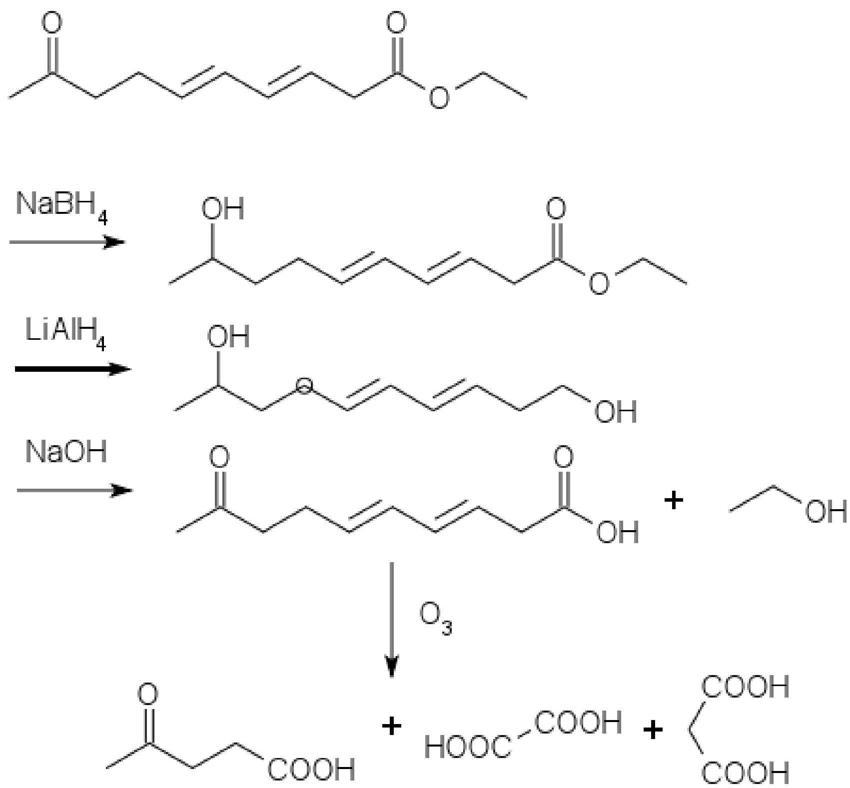


Product

Problem 4 (Estonia)

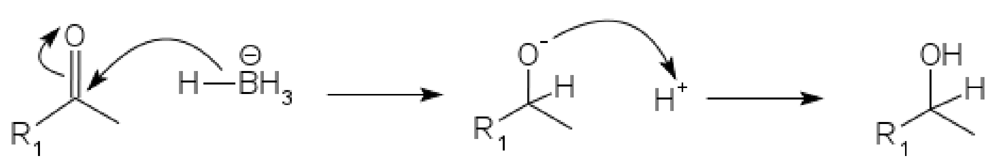
Some name for problem (6 points)

Solution Original compound is $CH_3COCH_2CH_2$-CH=CH-CH=CH-$CH_2COOCH_2CH_3$



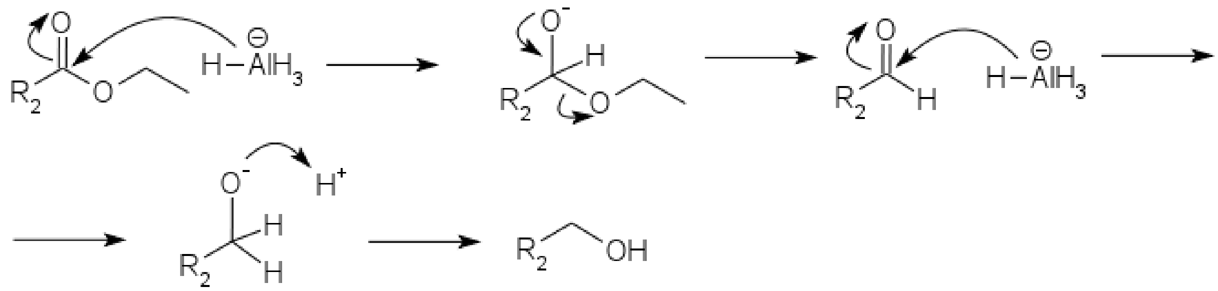
Mechanisms:

1)



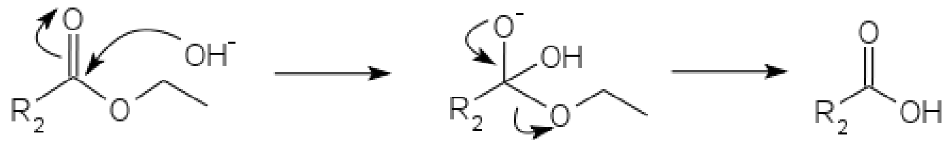
http://www.chem.ucalgary.ca/courses/351/Carey5th/Ch17/ch17-3-1-2.html

2)



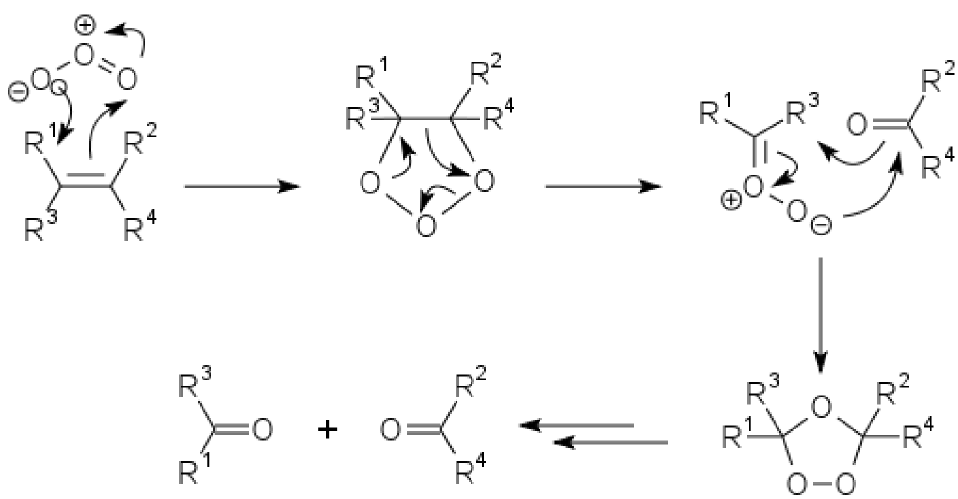
http://www.mhhe.com/physsci/chemistry/carey5e/Ch20/ch20-3-3-2.html

3)



http://www.chemguide.co.uk/physical/catalysis/hydrolyse.html

4)



http://en.wikipedia.org/wiki/Ozonolysis