

Name:

Code:

2nd Nordic Chemistry Olympiad

Theoretical Problems

4th July 2017

Stockholm, Sweden

Instructions

- Write your name and country code on all pages.
- The test booklet consists of 7 tasks and 40 pages.
- You have 4 hours for the examination. Do not start until the "START" signal is given.
- Use only the ballpoint pen and the calculator that have been handed out.
- Read the entire task before you begin to solve it, as there may be important information at the end of the text that you need to use to solve the task.
- All results must be written within the boxes. Answers written outside the boxes will not be reviewed and corrected. If you need paper, use the back of the paper sheets.
- Show your calculations in the boxes. You will only get max points if you show your calculations.
- When you have finished the exam, you must pass the test booklet to the person in charge.
- You must stop writing when the "STOP" signal is given.
- Stay in your place until you are allowed to leave the room.

Constants and Formulae

Avogadro's constant, $N_A = 6.0221 \times 10^{23} \text{ mol}^{-1}$

Boltzmann constant, $k_B = 1.3807 \times 10^{-23} \text{ J K}^{-1}$

Universal gas constant, $R = 8.3145 \text{ J K}^{-1} \text{ mol}^{-1} = 0.08205 \text{ atm L K}^{-1} \text{ mol}^{-1}$

Speed of light, $c = 2.9979 \times 10^8 \text{ m s}^{-1}$

Planck's constant, $h = 6.6261 \times 10^{-34} \text{ J s}$

Faraday constant, $F = 9.64853399 \times 10^4 \text{ C}$

Mass of electron, $m_e = 9.10938215 \times 10^{-31} \text{ kg}$

Standard pressure, $P = 1 \text{ bar} = 10^5 \text{ Pa}$

Atmospheric pressure, $P_{\text{atm}} = 1.01325 \times 10^5 \text{ Pa} = 760 \text{ mmHg} = 760 \text{ torr}$

Zero of the Celsius scale, 273.15 K

1 picometer (pm) = 10^{-12} m ; $1 \text{ \AA} = 10^{-10} \text{ m}$; nanometer (nm) = 10^{-9} m

1 eV = $1.6 \times 10^{-19} \text{ J}$

1 amu = $1.66053904 \times 10^{-27} \text{ kg}$

Ideal gas equation: $PV = nRT$

Enthalpy: $H = U - PV$

Gibbs free energy: $G = H - TS$ $\Delta G = \Delta G^\circ + RT \ln Q$

$$\Delta G^\circ = -RT \ln K = -nFE_{\text{cell}}^\circ$$

Entropy change: $\Delta S = \frac{q_{\text{rev}}}{T}$, where q_{rev} is heat for the reversible process

$$\Delta S = nR \ln \frac{V_2}{V_1} \text{ (for isothermal expansion of an ideal gas)}$$

Nernst equation: $E = E^\circ + \frac{RT}{nF} \ln \frac{C_{\text{ox}}}{C_{\text{red}}}$

Energy of a photon: $E = \frac{hc}{\lambda}$

Lambert-Beer law: $A = \log \frac{I_0}{I} = \epsilon b C$

Integrated rate law

Zero order $[A] = [A]_0 - kt$

First order $\ln [A] = \ln [A]_0 - kt$

Second order $\frac{1}{[A]} = \frac{1}{[A]_0} + kt$

Arrhenius equation

$$k = Ae^{-E_a/RT}$$

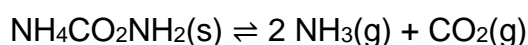
Periodic table of the elements with relative atomic masses and electronegativities

1	1,007,94																	2	4,0026																																		
H																		He																																			
2,1																																																					
3	6,941	4	9,0121																	5	10,811	6	12,011	7	14,007	8	15,999	9	18,998	10	20,180																						
Li		Be																		B		C		N		O		F		Ne																							
1,0		1,5																		2,0		2,5		3,0		3,5		4,0																									
11	22,990	12	24,305																	13	26,982	14	28,086	15	30,974	16	32,066	17	35,453	18	39,948																						
Na		Mg																		Al		Si		P		S		Cl		Ar																							
0,9		1,2																		1,5		1,8		2,1		2,5		3,0																									
19	39,098	20	40,078	21	44,956	22	47,87	23	50,942	24	51,996	25	54,938	26	55,845	27	58,933	28	58,993	29	63,546	30	65,39	31	69,723	32	72,61	33	74,922	34	78,96	35	79,904	36	83,80																		
K		Ca		Sc		Ti		V		Cr		Mn		Fe		Co		Ni		Cu		Zn		Ga		Ge		As		Se		Br		Kr																			
0,8		1,0		1,3		1,5		1,6		1,6		1,5		1,8		1,9		1,9		1,9		1,6		1,6		1,8		2,0		2,4		2,8																					
37	85,468	38	87,62	39	88,906	40	91,224	41	92,906	42	95,94	43	(97,907)	44	101,07	45	102,91	46	106,42	47	107,87	48	112,41	49	114,82	50	118,71	51	121,76	52	127,60	53	126,90	54	131,29																		
Rb		Sr		Y		Zr		Nb		Mo		Tc		Ru		Rh		Pd		Ag		Cd		In		Sn		Sb		Te		I		Xe																			
0,8		1,0		1,2		1,4		1,6		1,8		1,9		2,2		2,2		2,2		1,9		1,7		1,7		1,8		1,9		2,1		2,5																					
55	132,91	56	137,33	57	138,91	72	178,49	73	180,95	74	183,84	75	186,21	76	190,23	77	192,22	78	195,08	79	196,97	80	200,59	81	204,38	82	207,20	83	208,98	84	(209)	85	(210)	86	(222)																		
Cs		Ba		La		Hf		Ta		W		Re		Os		Ir		Pt		Au		Hg		Tl		Pb		Bi		Po		At		Rn																			
0,7		0,9		1,0		1,3		1,5		1,7		1,9		2,2		2,2		2,2		2,4		1,9		1,8		1,9		1,9		2,0		2,2																					
87	(223)	88	(226)	89	(227)	104	(261)	105	(262)	106	(263)	107	(262)	108	(265)	109	(266)																																				
Fr		Ra		Ac		Rf		Db		Sg		Bh		Hs		Mt																																					
0,7		0,7																																																			
																						58	140,12	59	140,91	60	144,24	61	(144,91)	62	150,36	63	151,96	64	157,25	65	158,93	66	162,50	67	164,93	68	167,26	69	168,93	70	173,04	71	174,97				
																						Ce		Pr		Nd		Pm		Sm		Eu		Gd		Tb		Dy		Ho		Er		Tm		Yb		Lu					
																						90	232,04	91	231,04	92	238,03	93	(237,05)	94	(244,06)	95	(243,06)	96	(247)	97	(247,07)	98	(251,08)	99	(252,08)	100	(257,1)	101	(258,1)	102	(259,1)	103	(262,1)	104	(267,1)	105	(278,10)
																						Th		Pa		U		Np		Pu		Am		Cm		Bk		Cf		Es		Fm		Md		No		Lr					

Problem 1**8 % of total**

a	b	c	d	e	f	Problem 1	%
10	10	10	10	10	10	60	8

Salt of hartshorn, used for baking cookies, consists of two salts: ammonium carbonate and ammonium carbamate. $\text{H}_4\text{CO}_2\text{NH}_2(\text{s})$ (ammonium carbamate) decomposes under heating to $\text{NH}_3(\text{g})$ and $\text{CO}_2(\text{g})$.



- a) Write the expression for the equilibrium constant for this reaction if no CO_2 or NH_3 are present from the beginning. Simplify the expression as much as possible.

$$K = (p^2(\text{NH}_3) \cdot p(\text{CO}_2)) / x(\text{NH}_4\text{CO}_2\text{NH}_2) = 4p^3(\text{CO}_2) \text{ or } p^3(\text{NH}_3) / 2$$

- b) Use the thermodynamic data given in the following table to calculate $\Delta_r H^\circ$ for the above reaction. Is the reaction endothermic or exothermic at standard conditions?

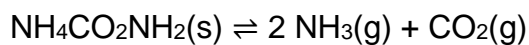
Compound	$\Delta_f H^\circ$ [kJ/mol]
$\text{NH}_4\text{CO}_2\text{NH}_2(\text{s})$	- 461.9
$\text{NH}_3(\text{g})$	45.9
$\text{CO}_2(\text{g})$	-393.5

$$\Delta_r H^\circ = 2 \Delta_f H^\circ(\text{NH}_3(\text{g})) + \Delta_f H^\circ(\text{CO}_2(\text{g})) - \Delta_f H^\circ(\text{NH}_4\text{CO}_2\text{NH}_2(\text{s}))$$

$$\Delta_r H^\circ = 2 \cdot 45.9 + (-393.5) - (-461.9) = 160.2 \text{ kJ/mol}$$

Answer: $\Delta_r H^\circ = 160.2 \text{ kJ/mol}$

In an experiment pure $\text{NH}_4\text{CO}_2\text{NH}_2$ and nothing else is in closed vessel. After some time, equilibrium is reached, the temperature being $40\text{ }^\circ\text{C}$



The total pressure in the vessel is recorded to 0.327 bar.

c) Calculate the partial pressure of CO_2 in vessel.

$$p(\text{total}) = 2 \cdot p(\text{NH}_3) + p(\text{CO}_2) = 0.327 \text{ bar} \Rightarrow p(\text{CO}_2) = 0.109 \text{ bar}$$

Answer: $P(\text{CO}_2) = 0.109 \text{ bar}$

d) Calculate the value of the equilibrium constant, K at $40\text{ }^\circ\text{C}$.

$$K = (p^2(\text{NH}_3) \cdot p(\text{CO}_2)) / x(\text{NH}_4\text{CO}_2\text{NH}_2) = 4p^3(\text{CO}_2) = 4(0.109)^3 = 0,00515 \text{ bar}^3$$

Answer: $K = 0,00515 \text{ bar}^3$

Originally 2,00 mol $\text{NH}_4\text{CO}_2\text{NH}_2(\text{s})$ was placed in the vessel, with the volume of 100 L at 40 °C..

- e) Calculate the amount of $\text{NH}_4\text{CO}_2\text{NH}_2(\text{s})$ present at equilibrium; assume that the volume of the solid substance can be neglected.

$$p(\text{CO}_2) = 0.109 \text{ bar}, n = \frac{pV}{RT} = \frac{0.109 \cdot 100}{0.08314 \cdot 313} = 0.42 \text{ mol}$$

$$n(\text{NH}_4\text{CO}_2\text{NH}_2) = 2.00 \text{ mol} - 0.42 \text{ mol} = 1.58 \text{ mol}$$

Answer: $n(\text{NH}_4\text{CO}_2\text{NH}_2) = 1.58 \text{ mol}$

$\Delta_r H^\circ$ for decomposing of 1 mol $\text{NH}_4\text{CO}_2\text{NH}_2(\text{s})$ was calculated under point **b**), if you don't have a result for $\Delta_r H^\circ$ then use the value 150.0 kJ/mol. The temperature was now raised to 50 °C.

- f) Calculate K at 50 °C, assuming that $\Delta_r H^\circ$ and $\Delta_r S^\circ$ is independent of temperature. If you miss parameter values that would have been obtained from previous part you can set these parameters to 1.

$$\ln K = -\frac{\Delta G}{RT} = \frac{-\Delta H}{RT} + \frac{\Delta S}{R} \text{ valid both at 40 °C and 50 °C. Subtraction gives:}$$

$$\ln \frac{K_{313}}{K_{323}} = \frac{-\Delta H}{R} \left(\frac{1}{313} - \frac{1}{323} \right) = \ln K_{323} + \frac{\Delta H}{R} \left(\frac{1}{313} - \frac{1}{323} \right) = \ln 0.00518 + \frac{160200}{8.314} \left(\frac{1}{313} - \frac{1}{323} \right)$$

$$\ln K_{323} = -5,263 + 19268 \cdot (0.0000989) = -3.357 \Rightarrow K_{323} = 0.0348 \text{ bar}^3$$

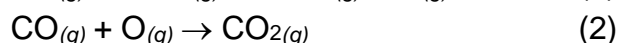
Answer: $K = 0.0348 \text{ bar}^3$

Problem 2

8 % of total

a	b	c	d	e	f	Problem 2	%
10	10	10	10	10	10		8

The oxidation of carbon monoxide to carbon dioxide in the gas phase is assumed to take place in two steps: The oxygen molecule dissociates into oxygen atoms, which then react with carbon monoxide.



The first step (1) is considered to be rate-limiting. The rate of reaction was measured for different partial pressures of CO and O₂ at 1250 °C. The values given in the table are the initial partial pressures of CO and O₂ and the time (in hours) that it took to lower the CO concentration by 0.1 mbar. Assume that initially there are no other gases present in the reaction vessel.

Experiment #	P _{O₂} (bar)	P _{CO} (bar)	t (h)
1	100	50	21.0
2	200	50	5.26
3	100	100	21.1

- a) Write the rate law for the reaction. Does it agree with the assumption that the first step is rate-limiting?

The reaction time is four times lower when the O₂ pressure is doubled => The rate law is second order with respect to O₂. The reaction time does not change (significantly) when the CO pressure is doubled => The rate law is zeroth order with respect to CO.

Rate law: $R = k (P_{\text{O}_2})^2$

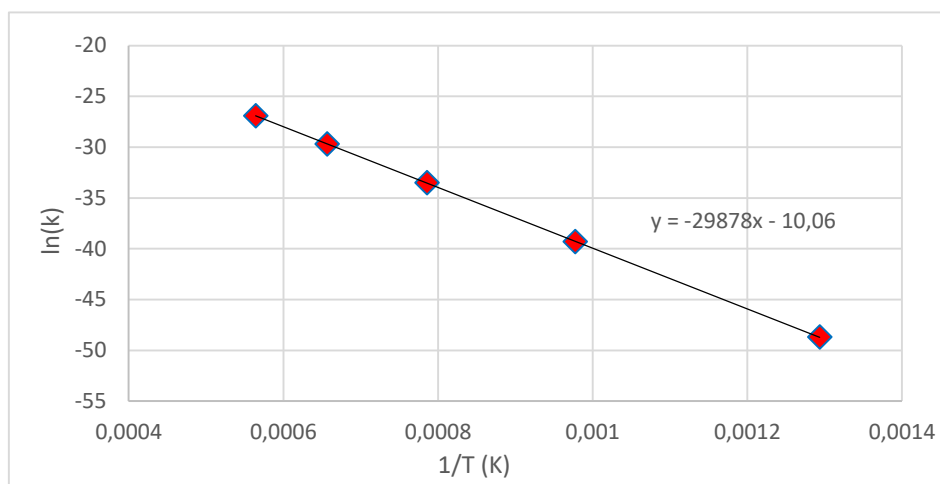
Are the rate law in agreement with the assumption that the first step is rate-limiting?

☒ Yes ☐ No

The rate constant of the reaction was measured in experiments at a series of temperatures. The results are given in the table below.

T (°C)	ln(k)
100	-90.3
500	-48.7
750	-39.3
1000	-33.5
1250	-29.7
1500	-26.9

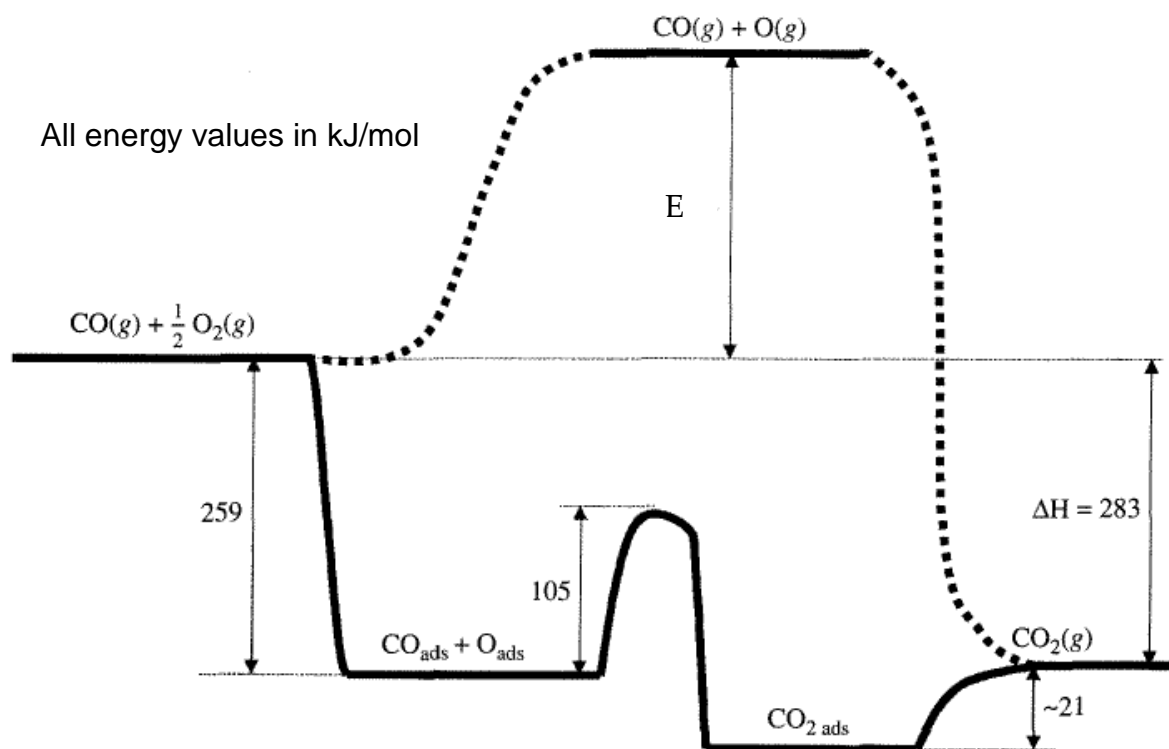
b) Use the experimental data to estimate the activation energy of the reaction.



The slope of the linear fit is approximately -29900 and this should be equal to $-E_a/R$. Therefore, we have $E_a = 249$ kJ/mol.

Answer: $E_a = 249$ kJ/mol

Experiments have shown that the oxidation of CO is much faster on some metal surfaces. Such catalysis has been used in catalytic converters for car exhaust. The proposed reaction mechanism is that (1) the two gas molecules are adsorbed on the metal surface, where (2) O_2 is dissociated and (3) CO_2 formed. The schematic figure below (based on data from Ertl, 1983) shows a schematic energy diagram for the oxidation of CO on a Pt(111) surface.



c) Which is the rate-limiting step in the catalysed reaction mechanism?

The second step, $\text{CO}_{\text{ads}} + \text{O}_{\text{ads}} \rightarrow \text{CO}_{2\text{ads}}$, may be assumed to be rate-limiting as it has the highest activation energy; $E_A = 105$ kJ/mol.

- d) Calculate the rate constant of the catalysed reaction at 100°C assuming that the pre-exponential factor is 10^{14} s^{-1} .

If $A = 10^{14} \text{ s}^{-1}$ and $E_a = 105 \text{ kJ/mol}$, then $k_{cat} = A \exp(-E_a/RT) = 0.198 \text{ s}^{-1}$ at 100°C.

Answer: $k_{cat} = 0.198 \text{ s}^{-1}$

- e) How much faster is the catalysed reaction at 100°C?

At 100°C we have

$$\ln(k) = -90.3 \Rightarrow \log_{10}(k) = -39.2 \text{ and } \ln(k_{cat}) = -1.6 \Rightarrow \log_{10}(k_{cat}) = -0.70.$$

Therefore, the catalysed reaction is about $10^{38.5}$ faster than the uncatalysed reaction.

Answer: $10^{38.5} = 3,16 \cdot 10^{38}$ times faster

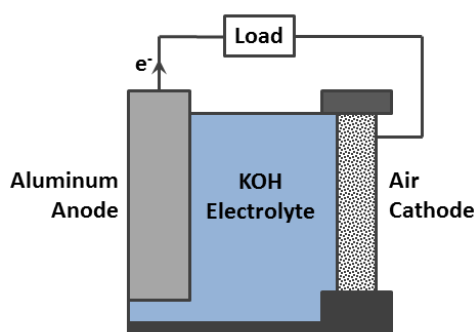
Problem 3

8 % of total

a	b	c	d	e	Problem 3	x%
10	10	10	10	10	50	8

Global warming and fossil fuel depletion increasingly place the development of sustainable energy systems at the top of political agendas around the world. Major investments in new energy technologies and systems to improve energy efficiency and reduce greenhouse gas emissions will continue to grow the coming decades. Some of the suggested technologies for energy production and energy storage are based on electrochemistry, i.e.: batteries, fuel cells, electrochemical solar cells, supercapacitors.

One promising alternative is a metal-air battery, i.e.: a hybride fuel cell.



Consider an aluminum-air battery, which is a light and very promising battery for carbon-free vehicles.

- a) The standard electrode reduction potential E^0 for aluminum is -1.66 V and for oxygen in an acidic water solution it is 1.23 V . What are the corresponding reactions at the anode and cathode respectively in acidic environment? What is the total cell reaction in an acidic environment? Note: The figure above shows the cell in basic environment.

Anode reaction: $\text{Al(s)} \rightleftharpoons \text{Al}^{3+} + 3\text{e}^-$

Cathode reaction: $\text{O}_2(\text{g}) + 4\text{H}^+ + 4\text{e}^- \rightleftharpoons 2\text{H}_2\text{O(l)}$

Cell reaction: $4\text{Al(s)} + 3\text{O}_2(\text{g}) + 12\text{H}^+ \rightleftharpoons 4\text{Al}^{3+} + 6\text{H}_2\text{O(l)}$

(Total reaction = 3 Cathode – 4 Anode)

b) Calculate the thermodynamic standard cell potential in acidic environment.

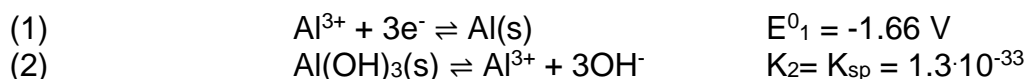
$$E^{\circ}_{\text{cell}} = 1.23 \text{ V} - (-1.66) \text{ V} = 2.89 \text{ V}$$

Answer: $E^{\circ}_{\text{cell}} = 2.89 \text{ V}$

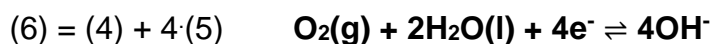
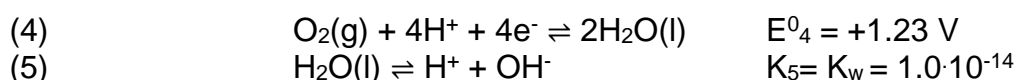
c) In practice the aluminum-air battery is often build with a basic electrolyte (e.g. KOH) in which solid aluminum hydroxide is formed and the reduction of oxygen occurs in basic water solution. What are the corresponding reactions at the anode and cathode respectively? What is the total cell reaction in a basic environment?

In basic environment (all half-reactions written as reductions):

The anode reaction is coupled the formation of aluminum hydroxide:



Cathode reaction in basic solution:



The total cell reaction = 3 Cathode – 4 Anode = 3(6) - 4(3):



Answers: Anode reaction: $\text{Al(s)} + 3\text{OH}^{-} \rightleftharpoons \text{Al(OH)}_3(\text{s}) + 3\text{e}^{-}$

Cathode reaction: $\text{O}_2(\text{g}) + 2\text{H}_2\text{O(l)} + 4\text{e}^{-} \rightleftharpoons 4\text{OH}^{-}$

Total reaction: $4\text{Al(s)} + 3\text{O}_2(\text{g}) + 6 \text{H}_2\text{O(l)} \rightleftharpoons 4 \text{Al(OH)}_3(\text{s})$

- d) Calculate the thermodynamic standard cell potential in a basic environment at 298K.

Hint: Coupled reactions occur at both electrodes which affect the cell potentials. The solubility product of aluminum hydroxide is $K_{sp}=1.3 \cdot 10^{-33}$ and water autoprotolysis ionization constant is $K_w=1.0 \cdot 10^{-14}$.

In general:

$$\Delta G^0 = -RT \ln K = -nFE^0$$

$$E^0 = RT/nF \ln K$$

For the coupled anode reaction (see answer (c))

$$\ln K_3 = \ln (K_1 K_2) = \ln K_1 + \ln K_2$$

and thus

$$\begin{aligned} E^0_3 &= RT/nF \ln K_1 + RT/nF \ln K_2 = E^0_1 + RT/nF \ln K_{sp} = \\ &= -1.66 \text{ V} + 8.314 \cdot 298 / (3 \cdot 96485) \ln (1.3 \cdot 10^{-33}) \text{ V} = \\ &= -1.66 \text{ V} - 0.65 \text{ V} = \mathbf{-2.31 \text{ V}} \end{aligned}$$

In similar way for the cathode reaction in basic environment

$$\ln K_6 = \ln (K_4 K_5^4) = \ln K_4 + 4 \ln K_5$$

and

$$\begin{aligned} E^0_6 &= RT/nF \ln K_3 + 4RT/nF \ln K_5 = E^0_3 + 4RT/nF \ln K_w = \\ &= 1.23 \text{ V} + 4 \cdot 8.314 \cdot 298 / (4 \cdot 96485) \ln (1.0 \cdot 10^{-14}) \text{ V} = \\ &= 1.23 \text{ V} - 0.83 \text{ V} = \mathbf{0.40 \text{ V}} \end{aligned}$$

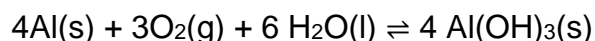
Finally the standard cell potential in basic environment:

$$E^0_{\text{cell}} = E^0_6 - E^0_3 = 0.40 \text{ V} - (-2.31 \text{ V}) = \mathbf{2.71 \text{ V}}$$

Answer: $E^0_{\text{cell}} = 2.71 \text{ V}$

- e) Is the real potential of the cell in basic environment higher or lower than the thermodynamic standard cell potential? Motivate your answer by showing the calculations in basic environment

The total cell reaction in basic environment is



The real cell potential is slightly lower than the standard potential since in air the oxygen partial pressure pushing the reaction (Le Chatelier's principle) is lower than the standard 1 bar. In air $p_{\text{O}_2} \approx 0.2$ bar.

From Nernst equation:

$$\begin{aligned} E_{\text{cell}} &= E_{\text{cell}}^0 - \frac{RT}{nF} \ln Q = \\ &= E_{\text{cell}}^0 - \frac{RT}{12F} \ln \left(\frac{\{\text{Al(OH)}_3\text{(s)}\}^4}{\{\text{Al(s)}\}^4 \{p_{\text{O}_2}\}^3 \{\text{H}_2\text{O(l)}\}^6} \right) \\ &= E_{\text{cell}}^0 - \frac{RT}{12F} \ln (1/(p_{\text{O}_2}/p^0)^3) \\ &= E_{\text{cell}}^0 + \frac{3RT}{12F} \ln (p_{\text{O}_2}/1\text{bar}) \\ &= E_{\text{cell}}^0 + \frac{RT}{4F} \ln (0.2) \\ &= 2.71\text{V} - 0.01\text{V} = 2.70\text{V} \end{aligned}$$

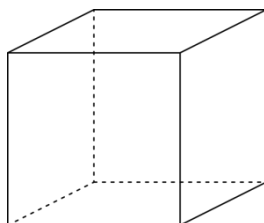
where the activity of pure condensed matter is one, e.g. $\{\text{Al(s)}\} = 1$.

Problem 4**9 % of total**

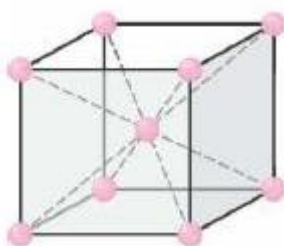
a	b	c	d	e	f	g	h	Problem 4	x %
10	10	10	10	10	10	10	10	80	9

Pure iron metal melts at 1811 K. Between room temperature and its melting point, iron metal can exist in different allotropic or crystalline forms. From room temperature to 1185 K, the crystal structure of iron metal exists as a body-centered cubic (bcc) lattice known as α -iron. Use the following data for this task: $M(\text{Fe}) = 55.847 \text{ g/mol}$, $M(\text{C}) = 12.011 \text{ g/mol}$, $N_A = 6.02214 \times 10^{23} \text{ /mol}$

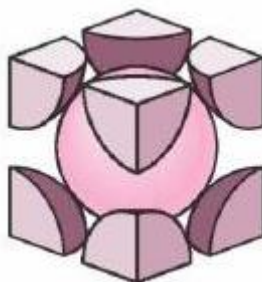
- a) Copy the general cube below and draw a sketch showing how atoms are distributed in a *bcc* lattice.



Several sketches are correct, e.g.



or



- b) How many atoms of iron are there per unit cell in a *bcc* cell?

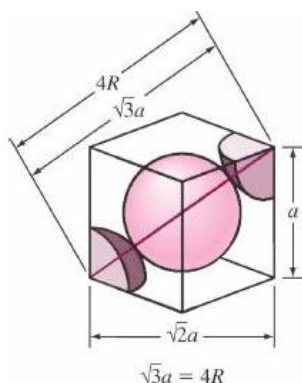
2 atoms (1 in centre of cell, and $8 \times 1/8$ per corner of cube)

- c) the density of pure iron metal is 7.874 g/cm^3 at 293 K . Calculate the atomic radius of iron (expressed in cm).

Two atoms of iron has a mass of $2 \times M(\text{Fe})$. The density is defined as $d = \text{mass/volume}$, where volume is $V = a^3$ where a is the dimension of the sides of the cube. Finally, the radius of the iron atom (R) is found to be 4 times the diagonal of the cube, which is given as $\sqrt{3}a$ (see figure below). Using this information,

$$V = (2 \cdot 55.847 \text{ g/mol} / 6.02214 \cdot 10^{23} \text{ 1/mol}) / 7.874 \text{ g/cm}^3 = 2.356 \cdot 10^{-23} \text{ cm}^3,$$

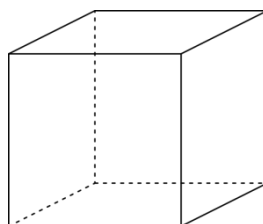
which gives $a = 2.867 \cdot 10^{-8} \text{ cm}$, and then $R = \sqrt{3}a/4 = 1.241 \cdot 10^{-8} \text{ cm}$.



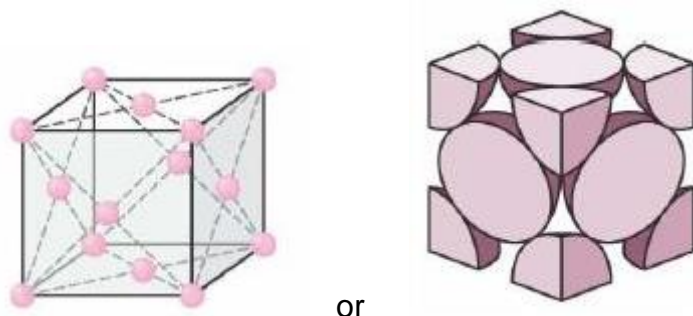
Answer: $r_{\text{Fe}} = 1.241 \cdot 10^{-8} \text{ cm}$

When heating iron from room temperature, a transition to a face-centered cubic (*fcc*) form, called γ -iron, takes place at 1185 K .

- d) Copy the general cube below and draw a sketch showing how atoms are distributed in a *fcc* lattice.



Several sketches are correct, e.g.



or

e) How many atoms of iron are there per unit cell in a *fcc* cell?

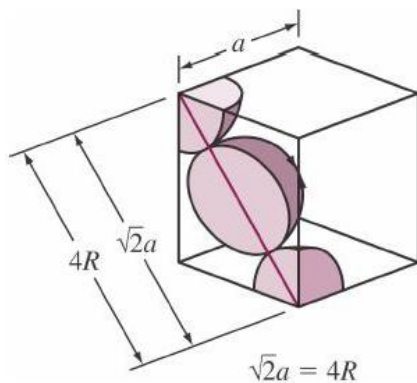
4 atoms (6 x 1/2 on each side, and 8 x 1/8 per corner)

f) Calculate the density of γ -iron (expressed in g/cm³). Note: Ignore any small effect due to the thermal expansion of the metal.

From the radius $R = 1.241 \cdot 10^{-8}$ cm the volume of the fcc cell is given by

$$V = a^3 = (4R/\sqrt{2})^3 = 4.327 \cdot 10^{-23} \text{ cm}^3 \text{ (see figure below).}$$

With 4 atoms per cell, the density becomes $d = (4 \cdot M(\text{Fe}) / N_A) / V = 8.573 \text{ g/cm}^3$.



Answer: Density of γ -iron = 8.573 g/cm³

Steel is an alloy of iron and carbon in which some of the interstitial spaces ("holes") of the crystal lattice (iron) are occupied by small atoms (carbon). The carbon content in steel typically ranges from 0.1 % to 4.0 %. In a blast-furnace, the melting of iron is facilitated when it contains 4.3 % of carbon by mass. If this mixture is cooled too rapidly the carbon atoms remain dispersed within the α -iron phase. This new solid, called martensite, is extremely hard and brittle. The size of the unit cell of martensite is the same as that of α -iron (*bcc*). Assume that the carbon atoms are evenly distributed in the iron structure

- g) Calculate the average number of carbon atoms per unit cell of α -iron in martensite containing 4.3 % C by mass.

100 g martensite contains 4.3 g C and 95.7 g Fe,

which corresponds to 0.36 mol C and 1.71 mol Fe,

and thus the ratio Fe : C is 4.8 : 1, or 0.21 C-atoms per Fe-atom.

Since there are 2 Fe atoms per *bcc* cell, there are on average 0.42 C-atoms per unit cell.

Answer: Average number of carbon atoms per unit cell = 0.42

h) Calculate the density (expressed in g/cm³) of this material.

The total mass of material per *bcc* cell in martensite is

$$(2 \cdot M(\text{Fe}) + 0.42 M(\text{C})) / N_{\text{A}} =$$

$$= (2 \cdot 55.847 \text{ g/mol} + 0.42 \cdot 12.011 \text{ g/mol}) / 6.02214 \cdot 10^{23} \text{ 1/mol} =$$

$$= 1.9385 \cdot 10^{-22} \text{ g material.}$$

$$\text{The density of martensite is } d = m / V = 1.9385 \cdot 10^{-22} \text{ g} / 2.356 \cdot 10^{-23} \text{ cm}^3 =$$

$$= 8.228 \text{ g/cm}^3.$$

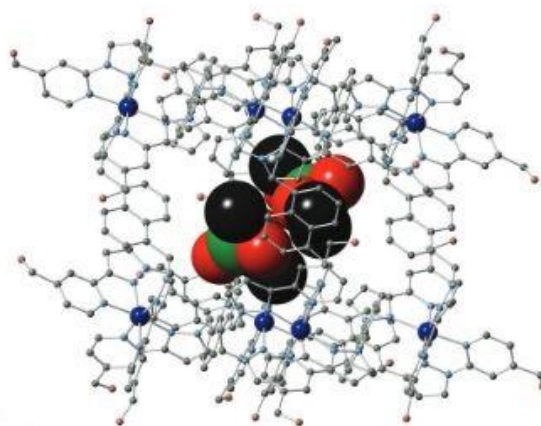
Answer: Density = 8.228 g/cm³.

Problem 5

9 % of total

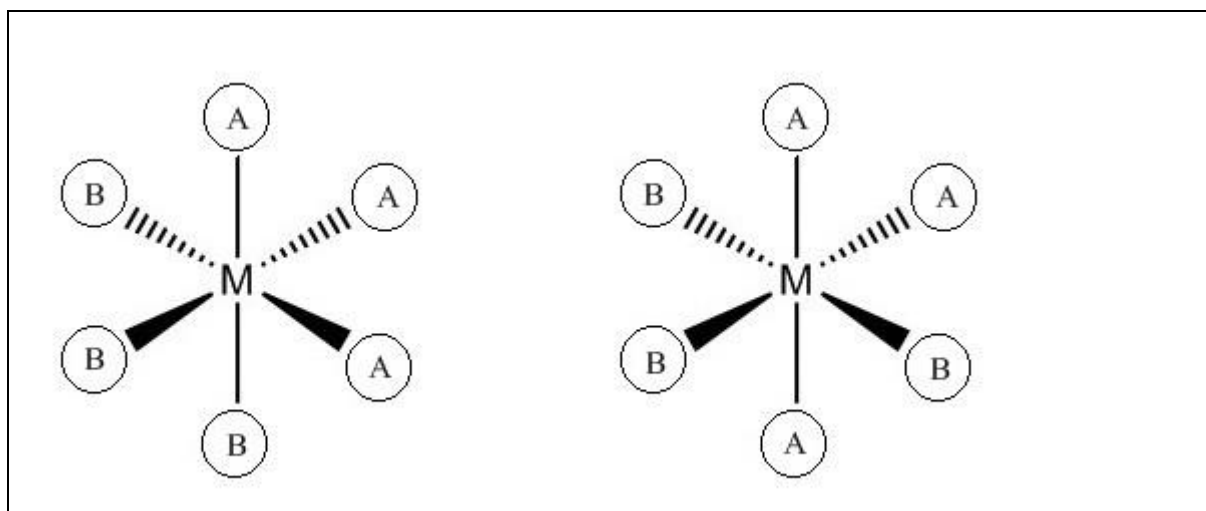
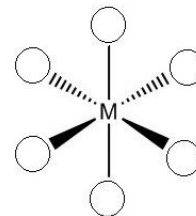
a	b	c	d	e	f	g	h	Problem 5	%
10	10	10	10	10	10	10	10	80	9

The most recent use of chemical warfare agents, CWA, was in Syria this year. Methods for the destruction of CWAs exist and involves strong oxidants. This problem will deal with some aspects of a new potential method for trapping CWAs by means of coordination cages, using only mild conditions as developed by Michael D. Ward and published 2016. A coordination cage is a supramolecular assembly of metal ions and ligands and have shown to trap other molecules within the available space in the cage, e.g. CWAs.



A coordination cage trapping a guest molecule.

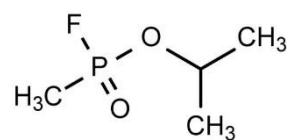
- a) If two different ligands *A* and *B*, three of each kind, coordinates in an octahedral geometry, then what are the possible different isomers that exist? Use the following template and write *A* and *B* in the circles for all isomers.



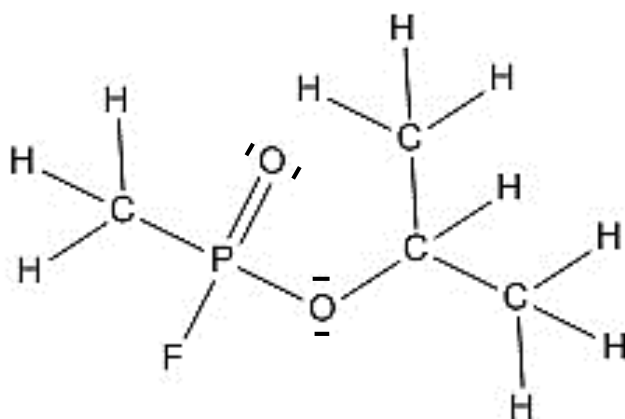
Name:

Code:

- b) Sarin is one of the most common chemical warfare agents. Write its full Lewis structure and state the geometry at the phosphorus center.

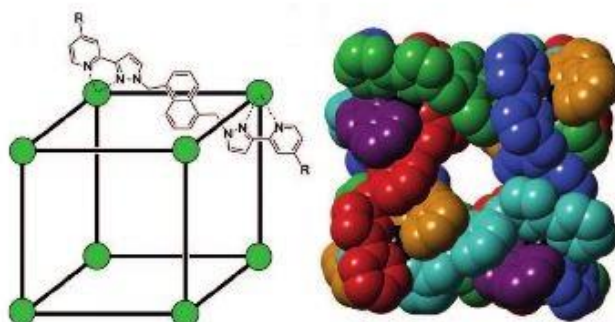
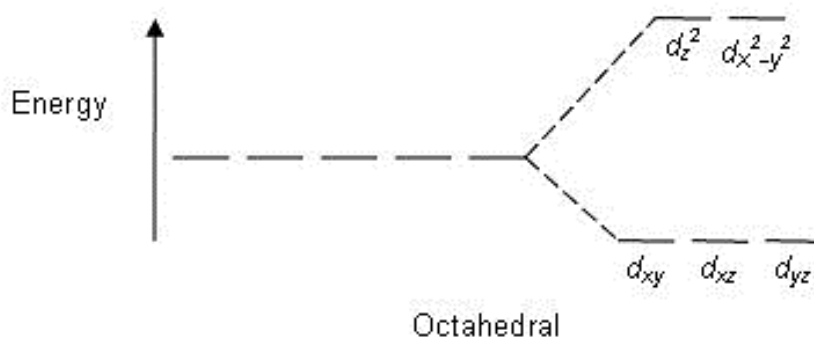


A sarin molecule

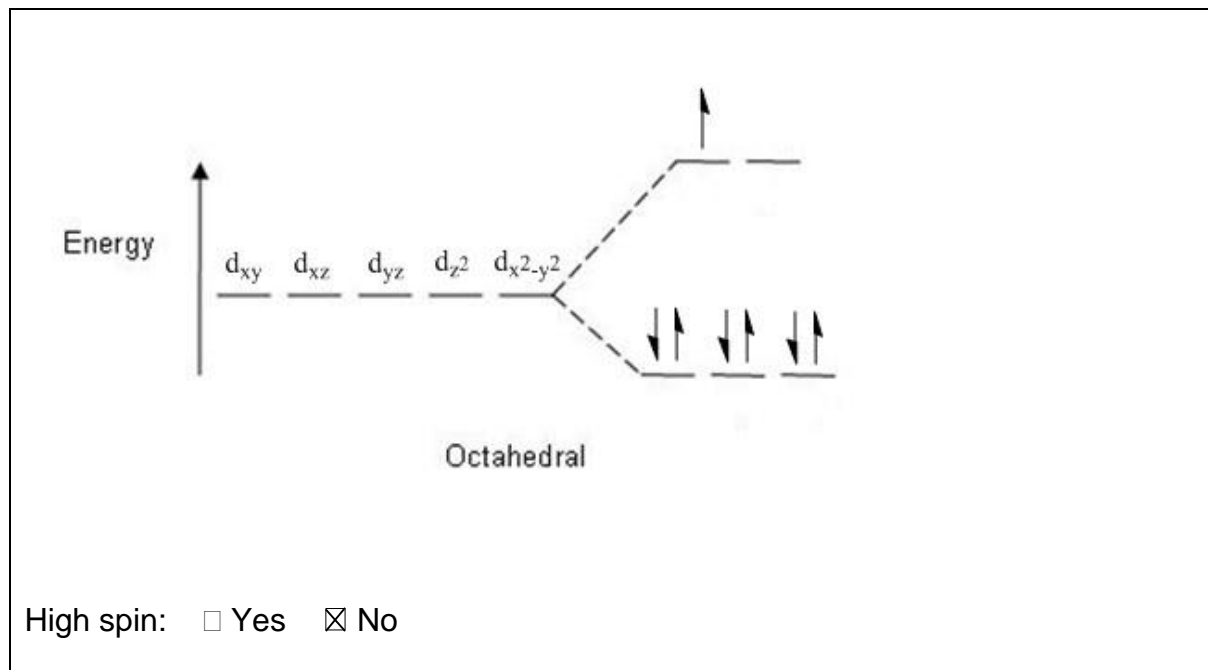


Geometry at the phosphorous center: Tetrahedral

- c) The crystal field-splitting diagram for an octahedral complex has two sets of energy levels, which *d*-orbitals corresponds to the different energy levels? Write the correct *d*-orbitals on the lines in the diagram.



- d) The coordination cage consists of 8 Co^{2+} ions and 12 ligands. *Each* metal ion center is an octahedral coordination complex. If the ligands are high field, to the far right in the spectrochemical series, then what is the electron configuration? Draw arrows to denote an electron and its spin in the splitting diagram in this case. Is the complex high-spin or low-spin?



- e) How many electrons does each Co^{2+} center have in its valence shell? Mark with a cross in the correct box.

i) ☐ 16 ii) ☐ 17 iii) ☐ 18 iv) ☒ 19 v) ☐ 20

- f) These cages can also be constructed with Cd^{2+} ions. Mark the correct property for these coordination centers.

i) ☐ High-spin ii) ☐ Low-spin iii) ☒ Neither of i) and ii

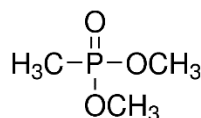
The equilibrium reactions that describes how a coordination host cage, Co-H, takes up DMMP molecules can be written as:



Where Co-H: Host cage with Co metal ions.

K : Equilibrium constant.

DMMP: Dimethyl methylphosphonate.
A model substance for a CWA



molecule.

A DMMP molecule

- g) In acetonitrile solution there is only possible for the cage to take up one DMMP molecule. The equilibrium constant at 298 K is $K_1 = 4.0 \text{ M}^{-1}$. Calculate the molar concentration of free DMMP molecules in a solution with the following initial concentrations $[\text{Co-H}]_{\text{initial}} = 0,100 \text{ M}$ and $[\text{DMMP}]_{\text{initial}} = 1.00 \cdot 10^{-6} \text{ M}$.



$$K_1 = \frac{x}{(0,100-x)(1,00 \cdot 10^{-6}-x)} = 4.0 \text{ M}^{-1}$$

Assume $x \ll 0,100$ then

$$K_1 = \frac{x}{(0,100)(1,00 \cdot 10^{-6}-x)} = 4.0 \text{ M}^{-1}$$

$$1.4x = 4.0 \cdot 10^{-7} \Rightarrow x = 2.86 \cdot 10^{-7} \text{ M}$$

$$[\text{DMMP}] = (1.00 \cdot 10^{-6} - 2.86 \cdot 10^{-7}) = 7.14 \cdot 10^{-7} \text{ M}$$

$$[\text{DMMP}] = 7.1 \cdot 10^{-7} \text{ M}$$

Answer: $[\text{DMMP}] = 7,1 \cdot 10^{-7} \text{ M}$

- h) In water the Co-H cage can take up two DMMP molecule. The equilibrium constants at 298 K is $K_1 = K_2 = 7.0 \text{ M}^{-1}$. W. An aqueous solution can be purified from DMMP by extraction, where Co-H-DMMP and Co-H-(DMMP)₂ are selectively and repeatedly removed from the solution. Calculate the percentage of DMMP molecules that have been removed during the first purification step when $[\text{Co-H}]_{\text{initial}} = 0.100 \text{ M}$ and $[\text{DMMP}]_{\text{initial}} = 1.00 \cdot 10^{-8} \text{ M}$.

$$[\text{DMMP}] + [\text{Co-H-DMMP}] + 2[\text{Co-H-(DMMP)}_2] = [\text{DMMP}]_{\text{initial}} = 1.0 \cdot 10^{-8} \text{ M} \quad (1)$$

Assume that $[\text{Co-H}]_{\text{initial}} = [\text{Co-H}] = 0.100 \text{ M}$

$$\frac{[\text{Co-H-DMMP}]}{[\text{Co-H}][\text{DMMP}]} = K_1 = 7.0 \text{ M}^{-1} \Rightarrow [\text{Co-H-DMMP}] = 7.0[\text{Co-H}][\text{DMMP}]$$

$$= 7.0 \cdot 0.100 \cdot [\text{DMMP}] = 0.7[\text{DMMP}] \Rightarrow$$

$$[\text{Co-H-DMMP}] = 0.7[\text{DMMP}] \quad (2)$$

$$\frac{[\text{Co-H-(DMMP)}_2]}{[\text{Co-H-DMMP}][\text{DMMP}]} = K_2 = 7.0 \text{ M}^{-1} \Rightarrow$$

$$[\text{Co-H-(DMMP)}_2] = 7.0[\text{Co-H-DMMP}][\text{DMMP}]$$

$$\text{Use equation (2)} \Rightarrow [\text{Co-H-(DMMP)}_2] = 7.0 \cdot 0.7[\text{DMMP}][\text{DMMP}] \Rightarrow$$

$$[\text{Co-H-(DMMP)}_2] = 4.9[\text{DMMP}]^2 \quad (3)$$

Equations (2) and (3) in (1):

$$[\text{DMMP}] + 0.7[\text{DMMP}] + 2 \cdot 4.9[\text{DMMP}]^2 = 1.00 \cdot 10^{-8} \Rightarrow$$

$$1.7[\text{DMMP}] + 9.8[\text{DMMP}]^2 = 1.00 \cdot 10^{-8} \Rightarrow$$

$$[\text{DMMP}] (1.7 + 9.8[\text{DMMP}]) = 1.00 \cdot 10^{-8}$$

$$\text{Assume that } 9.8[\text{DMMP}] \ll 1.7 \Rightarrow [\text{DMMP}] = \frac{1.00 \cdot 10^{-8}}{1.7}$$

$$\text{DMMP removed} = \frac{[\text{DMMP}]_{\text{initial}} - [\text{DMMP}]}{[\text{DMMP}]_{\text{initial}}} =$$

$$= \frac{1.00 \cdot 10^{-8} - \frac{1.00 \cdot 10^{-8}}{1.7}}{1.00 \cdot 10^{-8}} = 41.2 \%$$

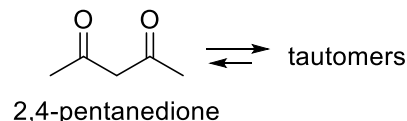
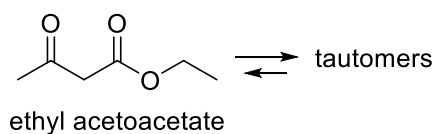
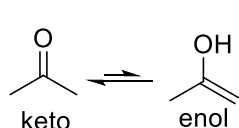
Percentage of DMMP removed: 41,2%

Problem 6

9 % of total

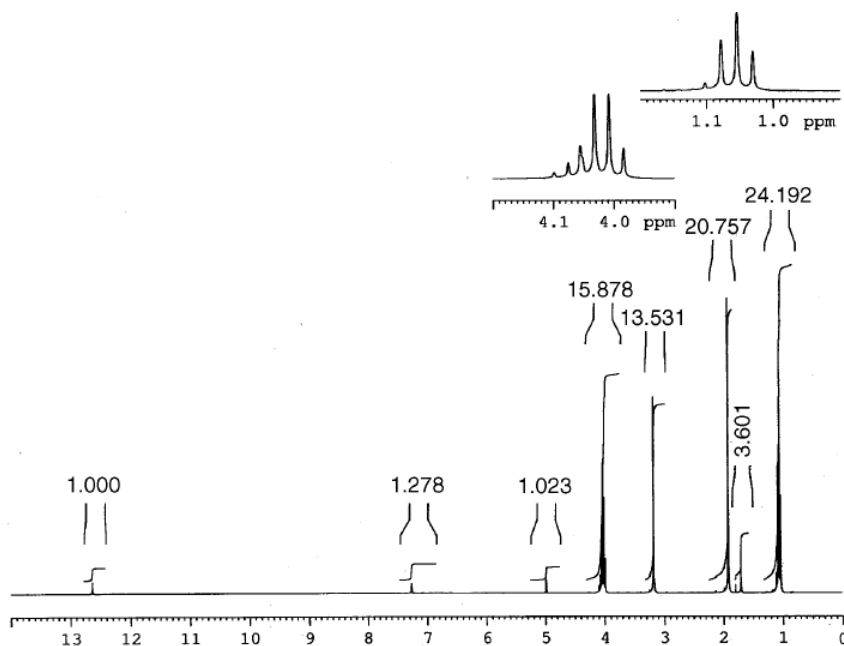
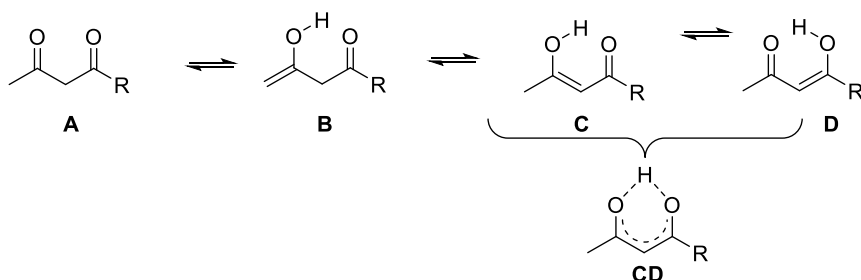
a	b	c	d	e	f	g	Problem 6	%
10	10	10	10	10	10	10	70	9

Carbonyl compounds are often in keto-enol equilibrium. The enol form is very important for carbonyl condensation reactions.



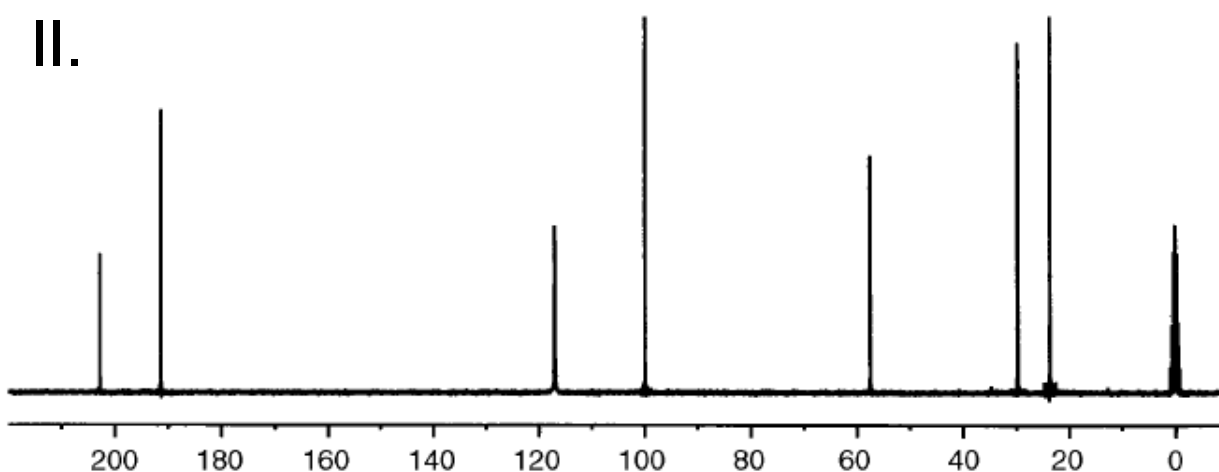
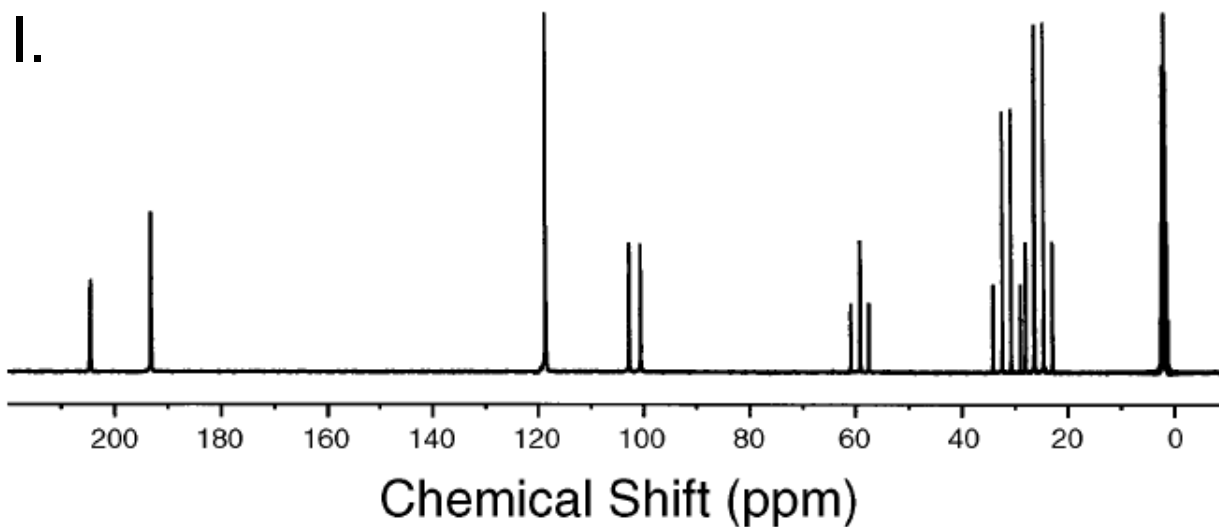
Ethyl acetoacetate and 2,4-pentanedione keto-enol tautomerism was studied with ^1H and ^{13}C NMR.

In theory, three different enol tautomers (**B-D**) can exist in solution (Benzene) for the ethyl acetoacetate. The **CD** is time-averaged structure that is commonly observed in NMR timescale.



^1H NMR spectrum of ethyl acetoacetate in C_6D_6 (residual signal 7.16ppm). The spectrum is integrated with values above the integral curves.

Corresponding situation can prevail for 2,4-pentanedione. The ^{13}C spectra have been measured in CD_3CN .



I: proton coupled and II: proton decoupled ^{13}C NMR spectrum of 2,4-pentanedione in CD_3CN (118.26 and 1.32 ppm)

Characteristic ^1H NMR Chemical Shifts

Type of Hydrogen (R=Alkyl, Ar=Aryl)	Chemical Shift (ppm)	Type of Hydrogen (R=Alkyl, Ar=Aryl)	Chemical Shift (ppm)
$(\text{CH}_3)_4\text{Si}$	0 (by definition)		
RCH_3	0.9	RCH=O	9.5-10.1
RCH_2R	1.2-1.4	RCOOH'	10-13
R_3CH	1.4-1.7	RCOCH_3	2.1-2.3
RCH_2I	3.2-3.3	RCOCH_2R	2.2-2.6
RCH_2Br	3.4-3.5	RCOOCH_3	3.7-3.9
RCH_2Cl	3.6-3.8	RCOOCH_2R	4.1-4.7
RCH_2F	4.4-4.5	$\text{R}_2\text{C=CRCHR}_2$	1.6-2.6
RCH_2NH_2	2.3-2.9	$\text{R}_2\text{C=CH}_2$	4.6-5.0
RCH_2OH	3.4-4.0	$\text{R}_2\text{C=CHR}$	5.0-5.7
RCH_2OR	3.3-4.0	$\text{RC}\equiv\text{CH}$	2.0-3.0
$\text{RCH}_2\text{CH}_2\text{OR}$	1.5-1.6	ArCH_3	2.2-2.5
R_2NH	0.5-5.0	ArCH_2R	2.3-2.8
ROH	0.5-6.0	ArH	6.5-8.5

Characteristic ^{13}C NMR Chemical Shifts

Type of Carbon (R=Alkyl, Ar=Aryl)	Chemical Shift (ppm)	Type of Carbon (R=Alkyl, Ar=Aryl)	Chemical Shift (ppm)
RCH_3	10-25	$\text{RC}(\text{triple bond})\text{CR}$	65-85
RCH_2R	20-35	RCH=CHR	120-140
R_3CH	25-35	ArylC	120-140
RCH_2COR	35-50	RCOOR	160-180
RCH_2Br	25-35	RCONR_2 (amide)	165-180
RCH_2Cl	40-45	RCOOH	175-185
RCH_2NH_2	30-65	RCHO	190-205
RCH_2OH	60-70	RCOR	200-215
RCH_2OR	65-70		

- a) How many ^1H NMR signals would ethyl acetoacetate tautomers **A**, **B**, **C** and **D** produce (ignore multiplicities)?

A: 4

B: 5

C: 5

D: 5

- b) How will the time averaging (**CD**) change the number of signals in the proton spectrum?

5 signals

- c) How many ^{13}C NMR signals would 2,4-pentanedione tautomers **A**, **B**, **C** and **D** produce.

A: 3

B: 5

C: 5

D: 5

- d) How will the time averaging (**CD**) change the number of signals in the carbon spectrum?

3 signals

- e) Interpret what tautomers (**A-D**) can be identified in the ^1H NMR spectrum. (or possibly mixtures of minor and major). Identify characteristic signals.

Minor tautomer(s): **CD**. Characteristic signals: 12.70, 5.00 and 1.7 ppm

Major tautomer(s): **A**. Characteristic signals 1.90 and 3.2 ppm
[Ethyl ester: 1.05 and 4.02 ppm]

- f) Interpret what tautomers (**A-D**) can be identified in the ^{13}C NMR spectra above. (or possibly mixtures). Identify characteristic signals.

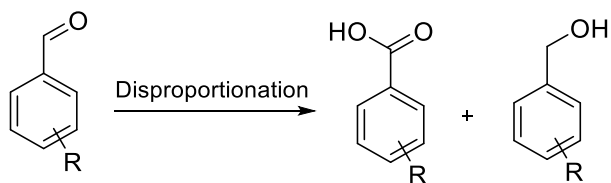
Again **A** and **CD** is considered.

The six signals arises from the tautomers.

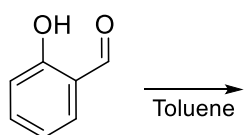
Ketone 205 ppm belongs to **A**, while averaged carbonyl gives 192 ppm.

100 ppm is **CD** enol methylene, while 58 ppm CH_2 of **A**.

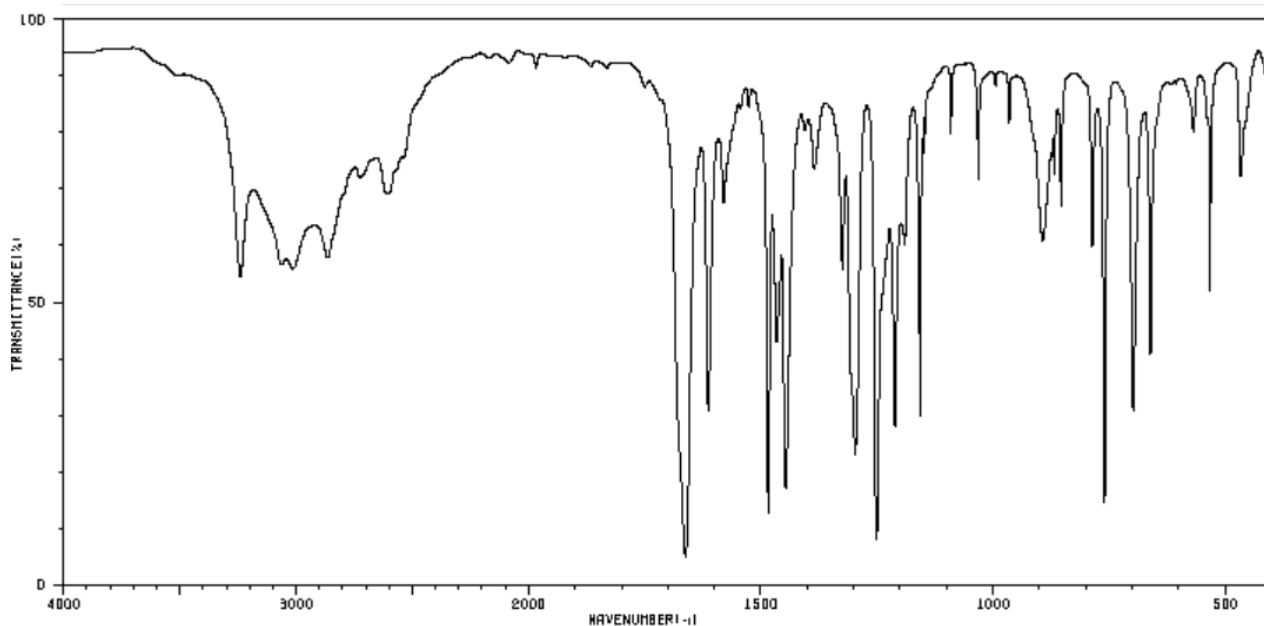
Disproportionation is a process where both oxidation and reduction takes place (bimolecularly) for single molecule yielding two products. In the case of (aromatic)aldehydes the process give alcohols and acid.



Question. Salicylaldehyde was stored extended periods of time in toluene. After isolation of compounds from the mixture four different IR spectra (**1-4**) could be recorded. Identify them i.e. find characteristic signals for each compound, by using the IR absorption frequencies tables.

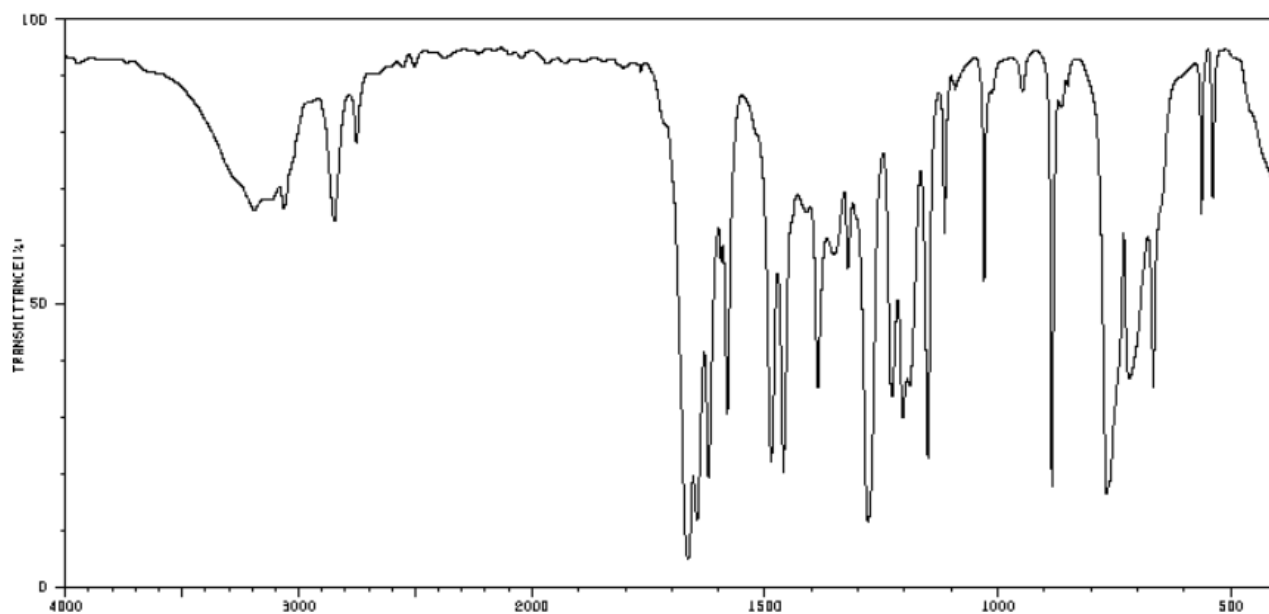


1.



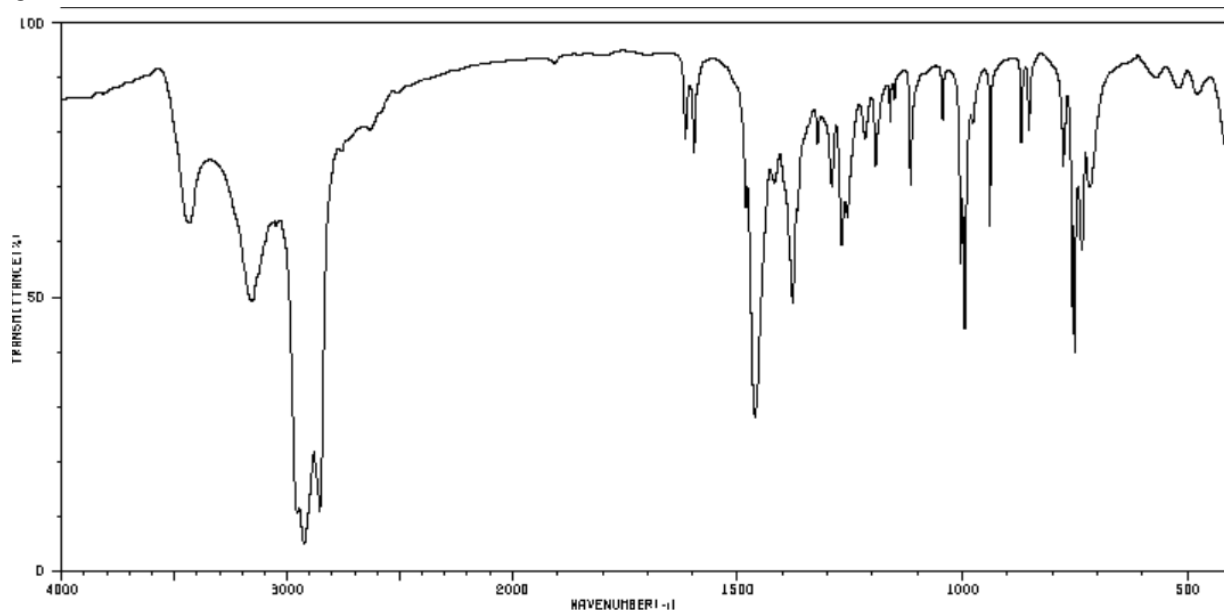
3240	62	1680	64	1325	63	1161	72	786	67
3013	53	1527	81	1297	21	1091	77	760	13
2864	55	1484	12	1251	7	1032	68	699	29
2724	70	1467	41	1239	49	966	79	661	38
2605	66	1447	16	1212	26	893	58	589	77
1662	4	1405	77	1190	58	868	70	533	50
1613	29	1386	70	1167	28	863	64	467	70

2.



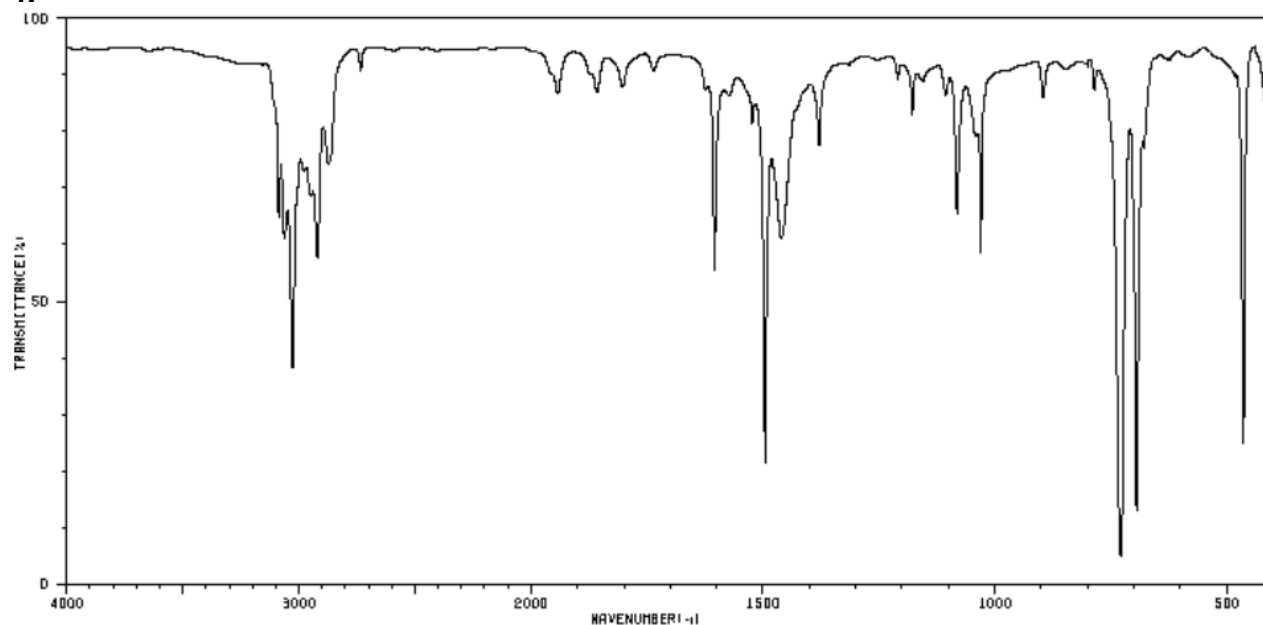
WAVENUMBER (cm⁻¹)					
3189	64	1696	66	1279	10
3064	64	1581	29	1228	32
2847	82	1487	21	1204	26
2762	74	1460	19	1190	34
1665	4	1387	33	1151	21
1645	11	1353	57	1114	80
1621	18	1322	63	1092	84
				1087	86
				1029	52
				1013	84
				947	84
				884	17
				864	81
				767	16
				718	36
				667	34
				563	64
				539	66

3.



3436	60	1697	72	1291	68	1116	68	862	77
3157	47	1482	64	1269	57	1044	79	776	70
2955	10	1461	26	1257	82	1004	53	757	46
2924	4	1418	68	1217	77	996	42	761	38
2855	10	1378	47	1194	70	977	79	735	57
1816	77	1367	64	1162	79	939	60	717	68
1606	84	1322	74	1162	81	870	74	621	84

4.



3087	62	1868	84	1210	86	896	81
3062	58	1803	84	1179	79	786	84
3028	37	1605	53	1156	86	729	4
2948	66	1624	79	1107	84	696	12
2920	55	1496	20	1082	62	678	74
2873	70	1461	58	1042	77	465	29
1942	84	1379	74	1030	67		

IR Absorption Frequencies Table

Characteristic IR Absorption Frequencies of Organic Functional Groups			
Functional Group	Type of Vibration	Characteristic Absorptions (cm⁻¹)	Intensity
Alcohol			
O-H	(stretch, H-bonded)	3200-3600	strong, broad
O-H	(stretch, free)	3500-3700	strong, sharp
C-O	(stretch)	1050-1150	strong
Alkane			
C-H	stretch	2850-3000	strong
-C-H	bending	1350-1480	variable
Alkene			
=C-H	stretch	3010-3100	medium
=C-H	bending	675-1000	strong
C=C	stretch	1620-1680	variable
Alkyl Halide			
C-F	stretch	1000-1400	strong
C-Cl	stretch	600-800	strong
C-Br	stretch	500-600	strong
C-I	stretch	500	strong
Alkyne			
C-H	stretch	3300	strong, sharp
-C≡C-	stretch	2100-2260	variable, not present in symmetrical alkynes
Amine			
N-H	stretch	3300-3500	medium (primary amines have two bands; secondary have one band, often very weak)
C-N	stretch	1080-1360	medium-weak
N-H	bending	1600	medium
Aromatic			
C-H	stretch	3000-3100	medium
C=C	stretch	1400-1600	medium-weak, multiple bands
Analysis of C-H out-of-plane bending can often distinguish substitution patterns			
Carbonyl			
C=O	stretch	1670-1820	strong
(conjugation moves absorptions to lower wave numbers)			
Ether			
C-O	stretch	1000-1300 (1070-1150)	strong

Nitrile			
CN	stretch	2210-2260	medium
Nitro			
N-O	stretch	1515-1560 & 1345-1385	strong, two bands

IR Absorption Frequencies of Functional Groups Containing a Carbonyl (C=O)			
Functional Group	Type of Vibration	Characteristic Absorptions (cm⁻¹)	Intensity
Carbonyl			
C=O	stretch	1670-1820	strong
(conjugation moves absorptions to lower wave numbers)			
Acid			
C=O	stretch	1700-1725	strong
O-H	stretch	2500-3300	strong, very broad
C-O	stretch	1210-1320	strong
Aldehyde			
C=O	stretch	1740-1720	strong
=C-H	stretch	2820-2850 & 2720-2750	medium, two peaks
Amide			
C=O	stretch	1640-1690	strong
N-H	stretch	3100-3500	unsubstituted have two bands
N-H	bending	1550-1640	
Anhydride			
C=O	stretch	1800-1830 & 1740-1775	two bands
Ester			
C=O	stretch	1735-1750	strong
C-O	stretch	1000-1300	two bands or more
Ketone			
acyclic	stretch	1705-1725	strong
cyclic	stretch	3-membered - 1850 4-membered - 1780 5-membered - 1745 6-membered - 1715 7-membered - 1705	strong
α,β -unsaturated	stretch	1665-1685	strong
aryl ketone	stretch	1680-1700	strong

- g) Identify the compounds and explain briefly your reasoning. (Remember that absolute IR stretching values differ to some extent from the tabularised ones due to interaction of functional groups)

The idea is to find characteristic signals that are aldehyde, OH and COOH stretching. One must then rationalize which spectra contain them and which not. The phenol signals makes the characterization more challenging while the OH hydrogen bonds effect on the hydrogen bond acceptor signals.

Spectrum **1**: Spectrum shows strong signal at ca. 1700 cm^{-1} . Compared to spectrum **2** there is one characteristic OH signal at 3200 cm^{-1} . This is salicylic acid spectrum.

Spectrum **2**: Spectrum shows also strong signal at ca. 1700 cm^{-1} . Less OH than above. This is salicylic aldehyde spectrum. (The hydrogen bonding shifts aldehyde vibration to unusually low frequency.)

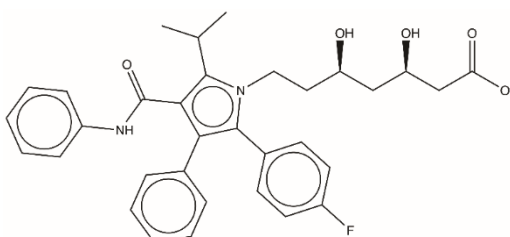
Spectrum **3**: No strong CO (ca. 1700 cm^{-1}) absorption, but broad signals in $3200\text{-}3600\text{ cm}^{-1}$. Compound is salicyl alcohol.

Spectrum **4**: No broad signals above 3000 cm^{-1} that are typical for OH, neither no strong C=O stretching signal for. This compound is toluene.

Problem 7

9 % of total

a	b	c	d	e	f	g	h	Problem 7	x %
10	10	10	10	10	10	10	10	80	9

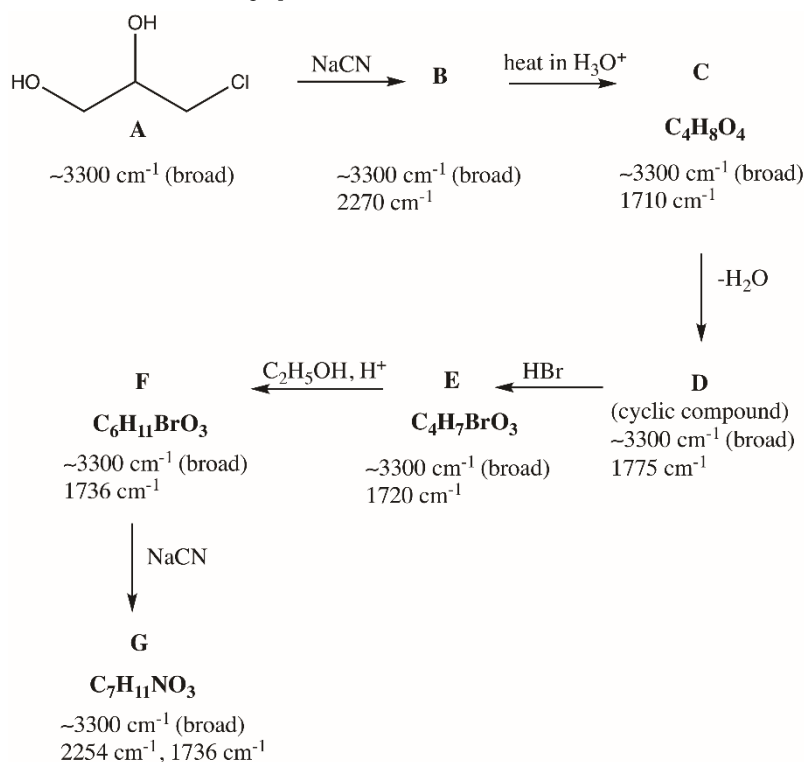


Pfizer's cholesterol-lowering drug Lipitor has been the best-selling pharmaceutical in the world. The active compound in Lipitor, atorvastatin, belongs to the drug class of statins. Atorvastatin acts by inhibiting a HMG-coA reductase in the liver which is involved in the production of cholesterol.

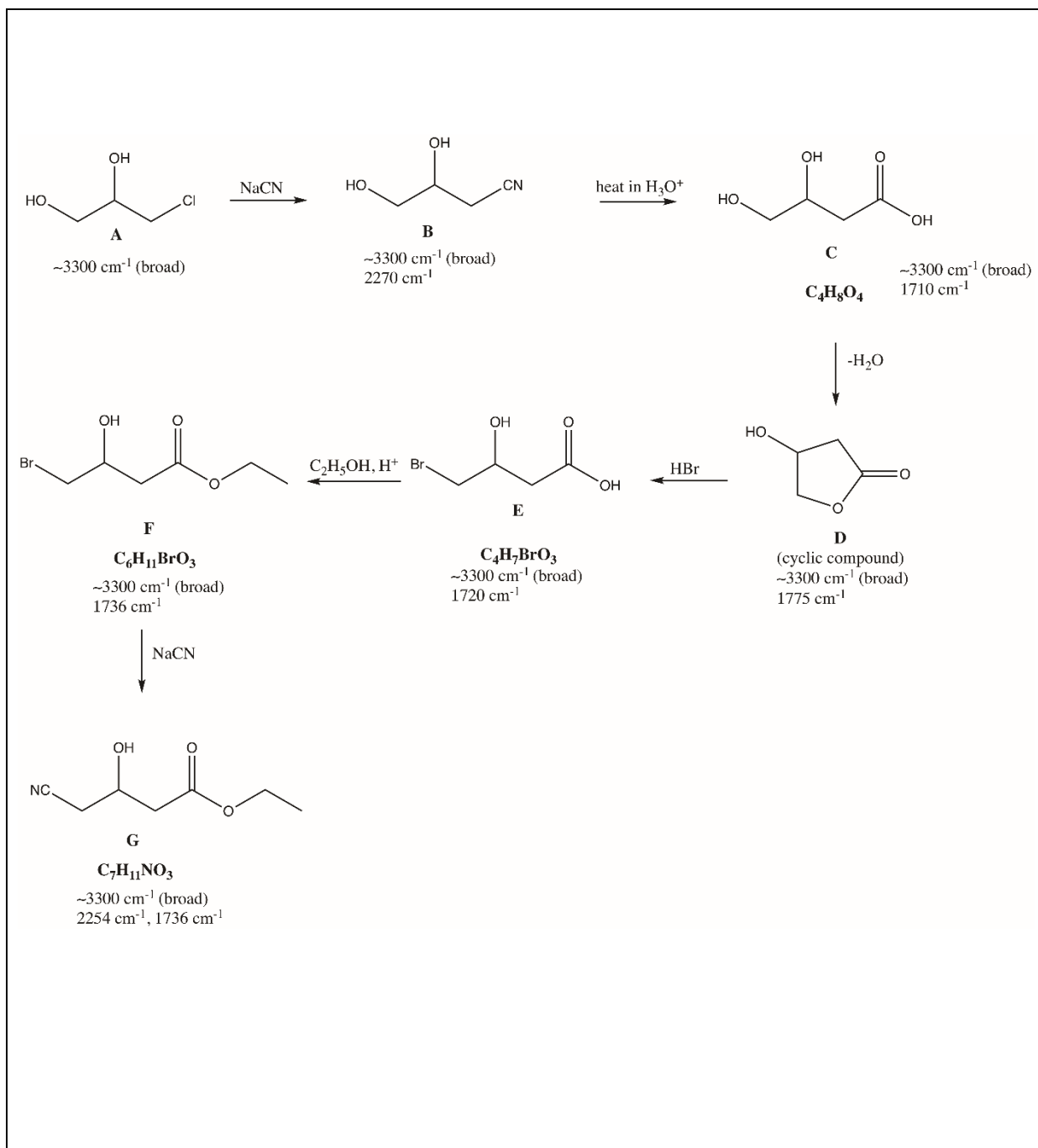
The first steps of a multi-stage synthesis of Lipitor are shown below.

Given in the boxes are the most characteristic IR stretching frequencies of the intermediates in the synthesis. No stretches due to any C–C or C–H bonds are included; stretching frequencies due to single bonds other than bonds to hydrogen do not show up in the range listed. You are not expected to know these stretching frequencies, but through careful reasoning, you should be able to use them to help work out the structures of the unknowns.

Note that not all the by-products are shown in the reaction schemes below



a) Give the structures for the compounds **B** to **G**.

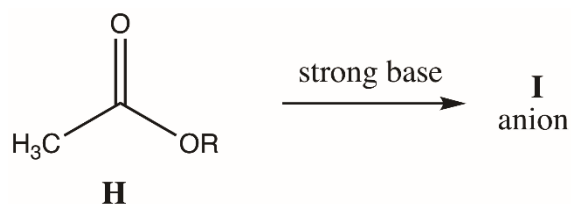


- b) Over the course of the whole question, complete the table of IR absorptions (*in the answer sheet*) found in compounds **A** to **M**.

Answer:

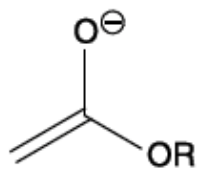
absorption / cm^{-1}	~ 3300 (broad)	1775	2250-2275	3374	1700-1740
bond	O-H	C=O in a small ring	C\equivN	N-H	C=O

Ester **H** is deprotonated by strong bases to give the reactive carbon nucleophile, anion **I**. The R group in the structure is an alkyl chain which remains unchanged throughout the entire synthesis.



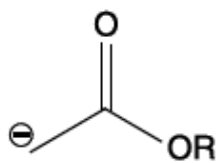
- c) Draw the structure for the anion **I**.

Anion **I**



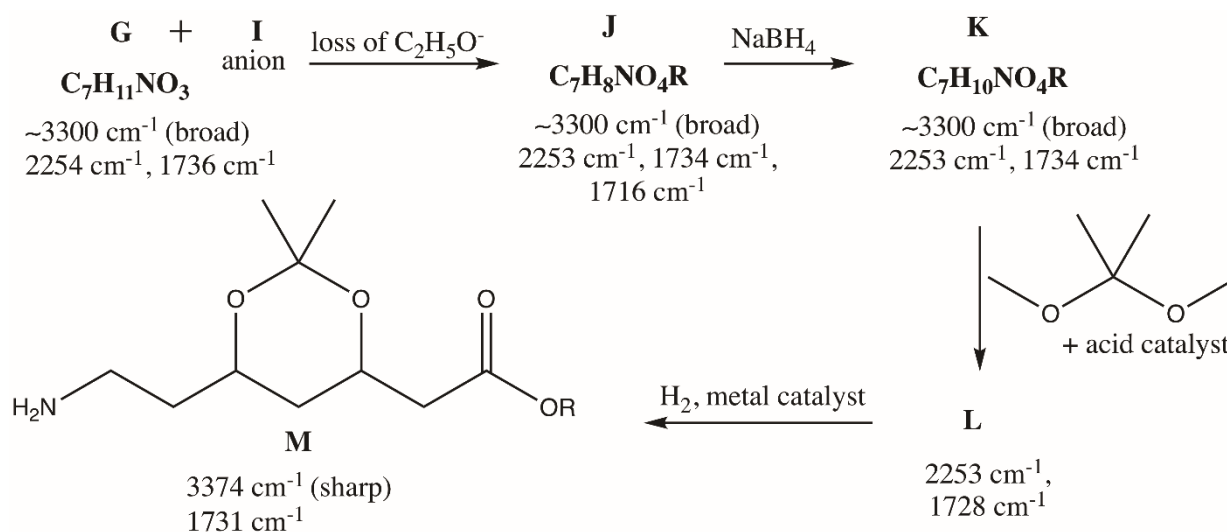
2 marks

or

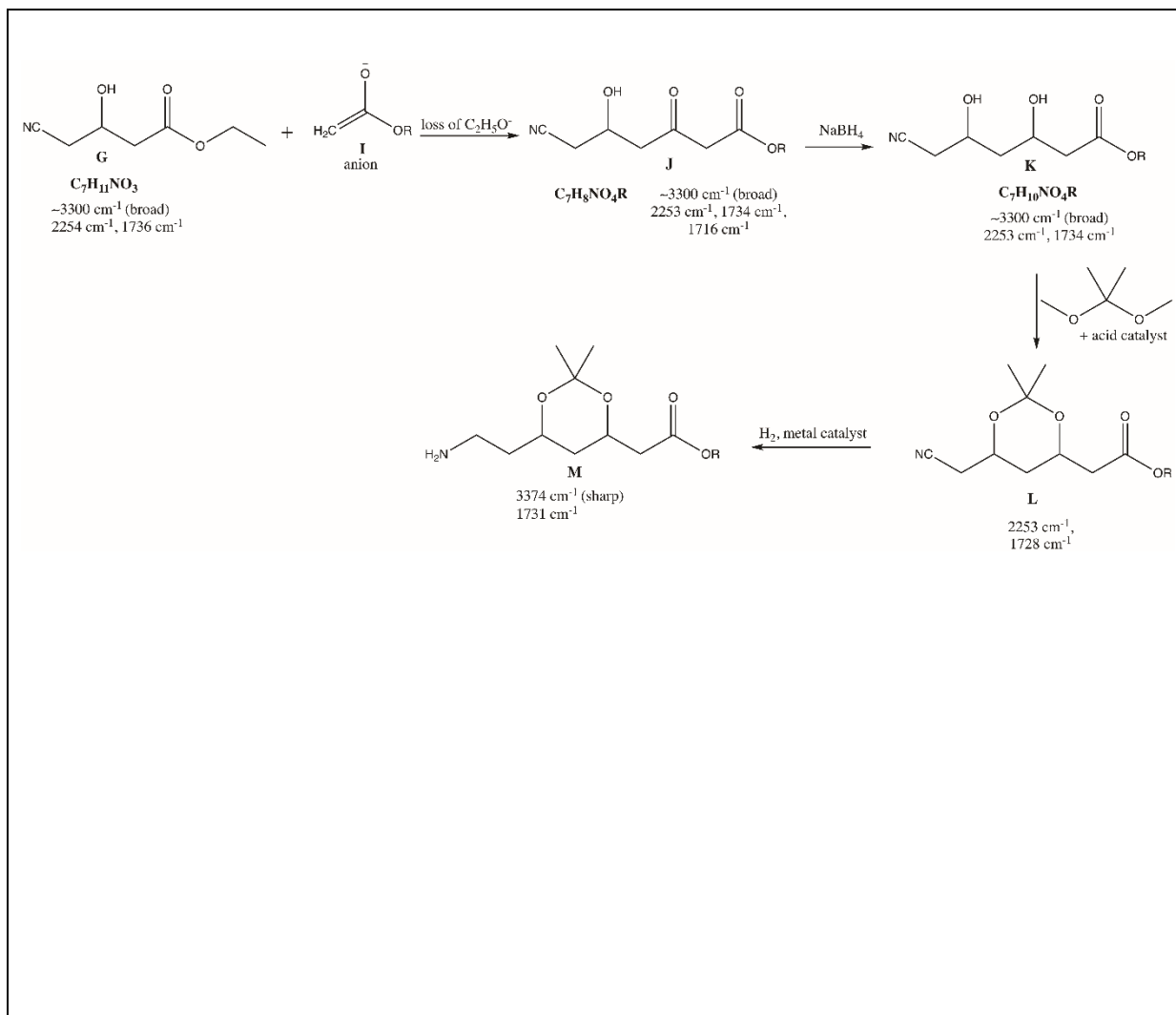


(1 mark for this alternative)

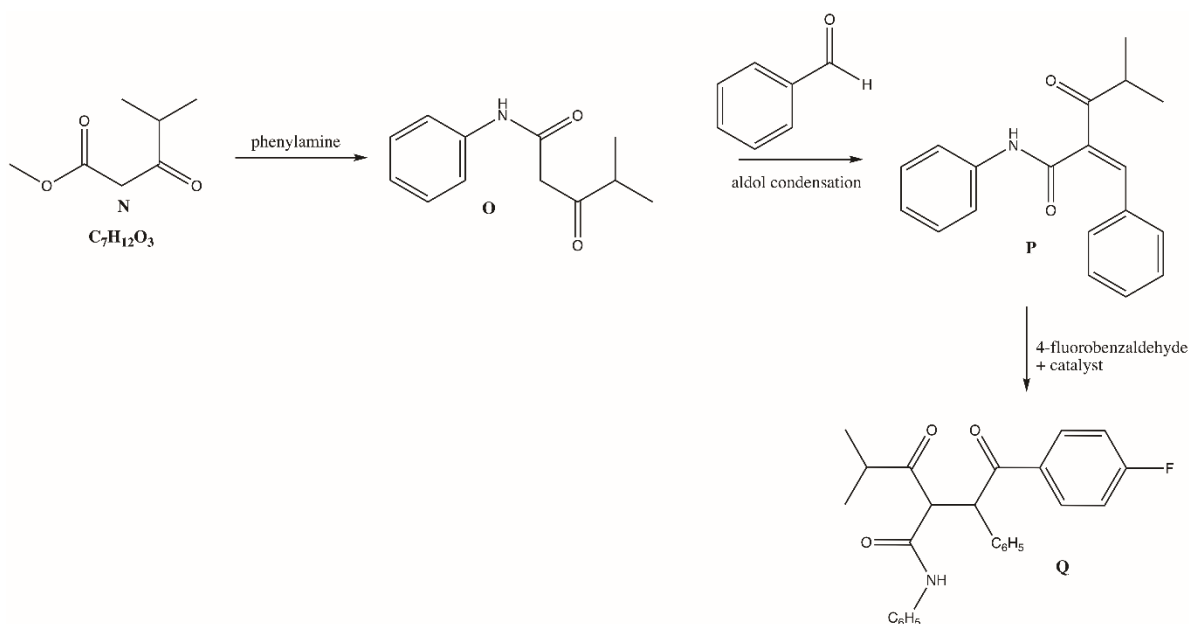
The synthesis continues as shown below:



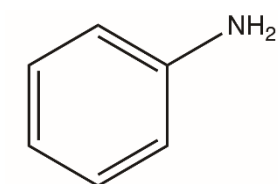
d) Give the structures for the compounds J, K and L.



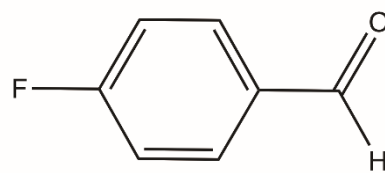
In a separate branch of the synthesis, **N** reacts with phenylamine to give compound **O**. This compound reacts with benzaldehyde in an aldol condensation to give compound **P**. **P** then reacts further with 4-fluorobenzaldehyde in the presence of a catalyst to give compound **Q**.



e) give the structures of phenylamine and 4-fluorobenzaldehyde.



phenylamine



4-fluorobenzaldehyde

The end of the problem set