The clouds of Venus · Solutions

1.1 (2pt)

☐ reaction 1	☐ reaction 2	☐ reaction 3	☐ reaction 4	☒ reaction 5	☐ reaction 6	☒ reaction 7

Marking note: 1 pt for each correct tick
0.5 point penalty for each incorrect tick

1.2 (2pt)

☒ A	☒ B	☐ C	☐ D	☐ E	☐ F

Marking note: 1 pt for each correct tick
0.5 point penalty for each incorrect tick

1.3 (8pt)

The molar mass of one of the substances,

$$\frac{16x}{0.533} = 30x$$

corresponds to NO when $x = 1$.

C, D, E, and F are all binary compounds. Furthermore, the oxidation of D (reaction 2) also yields another binary substance - an oxide. The difference between reaction 4 and the overall reaction is that, to form one mole of A, C requires an additional mole of oxygen atoms, whereas F requires only water. The following equation can be formulated:

$$\mathrm{M}(\mathbf{F}) = \mathrm{M}(\mathbf{C}) + 16$$

And based on the relationship,

$$\mathrm{M}(\mathbf{C}) + \mathrm{M}(\mathbf{E}) = \mathrm{M}(\mathbf{D}) + \mathrm{M}(\mathbf{F})$$

It is clear that the ratio

$$\mathrm{M}(\mathbf{E}) = \mathrm{M}(\mathbf{D}) + 16$$

is also valid.

In that case, NO can be either C or D, since these are the only two that can be oxidized by the addition of a single oxygen atom.

If we imagine that C is NO and try to formulate the overall reaction,

$$2\ \mathrm{NO} + 2\mathrm{H_2O} + \mathrm{O_2} \rightarrow 2\mathrm{H_2NO_3}$$

The result is an invalid product.

Hence,

D - NO and **E** - $\mathrm{NO_2}$

Another pair of oxides with a ratio

$$\mathrm{M}(\mathbf{F}) = \mathrm{M}(\mathbf{C}) + 16$$

is SO_2 and SO_3

Then, overall reaction will be

$$2SO_2 + 2H_2O + O_2 \rightarrow 2H_2SO_4$$

This is applicable to the reaction for producing sulfuric acid and to the overall process known as the chamber (or nitrous) method for sulfuric acid production.

And $NOHSO_4$ is suitable for **B**.

A - H_2SO_4	**B** - $NOHSO_4$	**C** - SO_2	**D** - NO	**E** - NO_2	**F** - SO_3

Marking note: 2 pt for each A and B
1 pt for each C-F

1.4 (1pt)

☐ **a)**	☒ **b)**	☐ **c)**	☐ **d)**

Marking note: 1 pt for correct tick
0.5 points penalty for each incorrect tick

1.5 (3pt)

$$T = 658 - 6.28 \times 60 = 281 \text{ K}$$

Every compound with a melting point higher than 281 K can be a solid

☒ **A**	☒ **B**	☐ **C**	☐ **D**	☐ **E**	☒ **F**

Marking note: 1 pt for each correct tick.
0.5 pt penalty for one incorrect tick.
1.5 pt penalty for two incorrect ticks.
3 pt penalty for three incorrect ticks.

1.6 (7pt)

(1) $2NOHSO_4 + SO_2 + 2H_2O \rightarrow 3H_2SO_4 + 2\ NO$
(2) $2\ NO + O_2 \rightarrow 2NO_2$
(3) $SO_2 + NO_2 \rightarrow SO_3 + NO$
(4) $SO_3 + H_2O \rightarrow H_2SO_4$
(5) $2SO_3 + H_2O + NO + NO_2 \rightarrow 2NOHSO_4$
(6) $2NOHSO_4 + H_2O \rightarrow NO + NO_2 + 2H_2SO_4$
(7) $NO + NO_2 + 2H_2SO_4 \rightarrow 2NOHSO_4 + H_2O$

Marking note: 1 pt for each correct reaction

Corannulene · Solutions

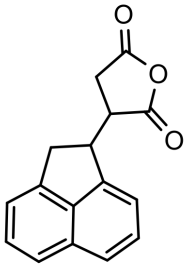
2.1 (6pt)

Type	C_2	C_3	C_4	C_5	C_6	σ	i
n	0	0	0	1	0	5	0

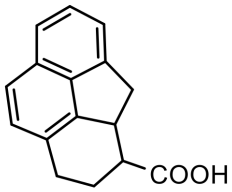
Marking note: 3 points for each correct number.
1 point penalty for each incorrect number.
Total cannot be negative

2.2 (32pt)

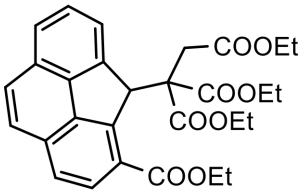
A



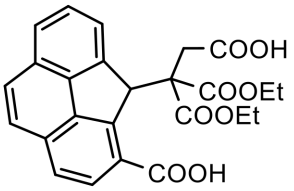
B



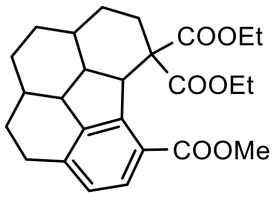
C



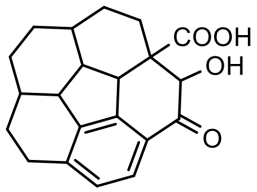
D



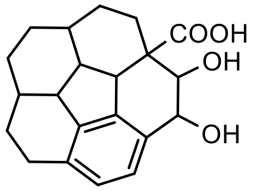
E



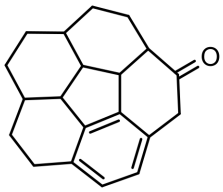
F



G



H



Marking note: 4 points for each correct structure.
1 point penalty for missing function group in the structure.

2.3 (3pt)

$\square\ \Delta G > 0$	$\square\ \Delta G < 0$	$\boxtimes\ \Delta G = 0$

Marking note: 3 points for correct tick

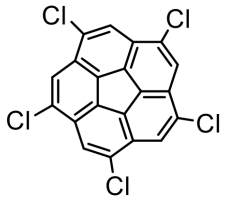
2.4 (9pt)

Type	C_2	C_3	C_4	C_5	C_6	σ	**i**
n	5	0	0	1	0	6	0

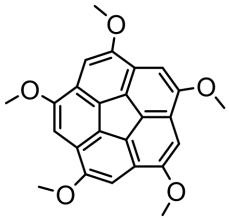
Marking note: 3 points for each correct number.
1 point penalty for each incorrect number.
Total cannot be negative

2.5 (12pt)

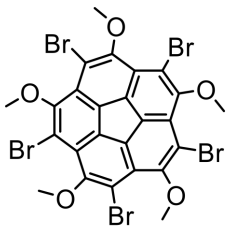
M



N



O



Marking note: 4 points for each correct structure.
1 point penalty for missing function group in the structure.

2.6 (6pt)

Each Cd ion requires 6 N atoms to coordinate and there are 15 N atoms in one tecton.

Overall

$$12 \times 15 = 180 \ \text{ N atoms}$$

So,

$$x = \frac{180}{6} = 30$$

x = 30

☐ a	☒ **b**	☐ c	☐ d

Marking note: 3 points for x
3 points for correct tick.

Chust at the elementary level · Solutions

3.1 (5pt)

Using the Bragg's law $n\lambda = 2d \cdot \sin\theta$, we find that,

$$d = \frac{1.5406}{2\sin\left(\frac{44.85}{2}\right)} = 2.019 \text{ Å}$$

but the parameter is not equal to the distance between the planes, $\frac{1}{d^2} = \frac{h^2+k^2+l^2}{a^2}$, thus, the parameter of cell is

$$a = d\sqrt{1^2+1^2+0^2} = 2.856 \text{ Å}$$

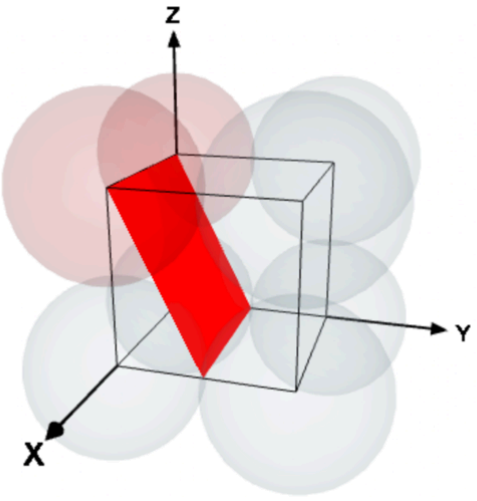
Through the atomic mass of Fe,

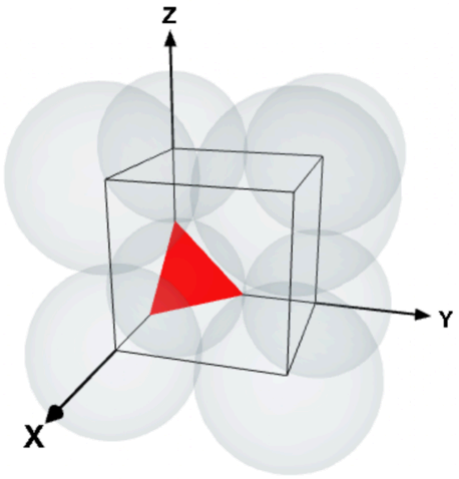
$$\rho = \frac{2 \cdot 55.8}{N_\text{A} \cdot (2.856 \cdot 10^{-8})^3} = 7.960 \text{g/cm}^3$$

Marking note: 1 pt for calculation of d.
1 pt for calculation of a.
1 pt for volume.
1 pt for correct number of atoms in lattice.
1 pt for atomic mass determination.

3.2 (6pt)

Planes (021) and (222) respectively:

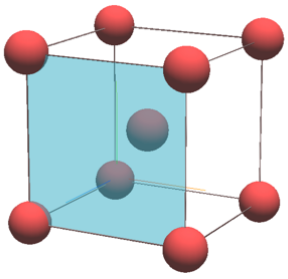


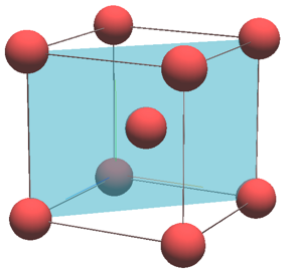


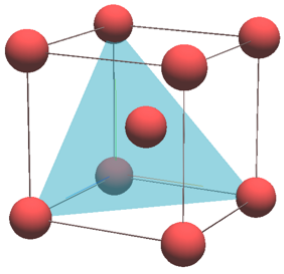
Marking note: 3 pt for each plane.
1 pt for correct intercept point on lattice in each axis.

3.3 (7pt)

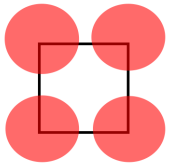
Planes (100), (110), (111) for the BCC lattice, respectively:







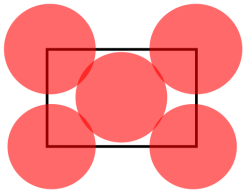
For (100):



Here $N = \frac{1}{4} \cdot 4 = 1$, which means

$$\text{PPD} = \frac{1}{2.856^2} = 0.12260 \text{Å}^{-2}$$

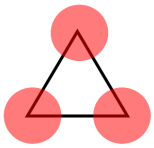
For (110):



Here $N = \frac{1}{4} \cdot 4 + 1 = 2$, thus

$$\text{PPD} = \frac{2}{\sqrt{2} \cdot 2.856^2} = 0.17338 \text{Å}^{-2}$$

For (111):



Here $N = \frac{1}{6} \cdot 3 = \frac{1}{2}$, thus

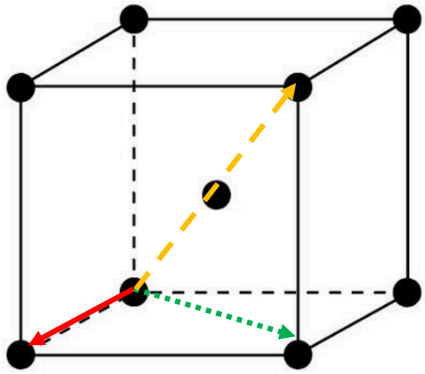
$$\text{PPD} = \frac{\frac{1}{2}}{\frac{\sqrt{3}\left(\sqrt{2} \cdot 2.866\right)^2}{4}} = 0.0708 \text{Å}^{-2}$$

Thus, the densest plane is (110) and the sliding occurs on this plane in iron at room temperature.

Marking note: 2 pt for each plane: 1 pt for N and 1 pt for final PPD.
1 pt for densest plane.

3.4 (7pt)

[100] – red, [110] – green, [111] – yellow are shown on the figure.



For BCC: $\mathrm{LPD}_{110} < \mathrm{LPD}_{100} < \mathrm{LPD}_{111}$.

Also, we can calculate these values as follows:

$$\mathrm{LPD}_{100} = \frac{1}{2.856} = 0.350\text{Å}^{-1}$$

$$\mathrm{LPD}_{110} = \frac{1}{2.856\sqrt{2}} = 0.248\text{Å}^{-1}$$

$$\mathrm{LPD}_{111} = \frac{2}{2.856\sqrt{3}} = 0.404\text{Å}^{-1}$$

Marking note: 2 pt for each direction: 1 pt for N and 1 pt for final LPD.
1 pt for ordering.

3.5 (15pt)

Full dislocation reaction equations

$$\frac{1}{2}[110] \rightarrow \frac{1}{6}[211] + \frac{1}{6}[12\bar{1}]$$

$$\frac{a}{2}[011] + \frac{a}{2}[10\bar{1}] \rightarrow \frac{a}{6}[110] + \frac{a}{6}[11\bar{2}] + \frac{a}{6}[112]$$

$$\frac{1}{2}[111] + \frac{1}{2}[1\bar{1}\bar{1}] \rightarrow [100]$$

To calculate energy change,

$$\left(\frac{1}{2}\sqrt{1^2+1^2+0^2}\right)^2 > \left(\frac{1}{6}\sqrt{2^2+1^2+1^2}\right)^2 + \left(\frac{1}{6}\sqrt{1^2+2^2+(-1)^2}\right)^2$$

$$\left(\frac{a}{2}\sqrt{0+1^2+1^2}\right)^2 + \left(\frac{a}{2}\sqrt{1^2+0+(-1)^2}\right)^2 > \left(\frac{a}{6}\sqrt{1^2+1^2+0^2}\right)^2 + \left(\frac{a}{6}\sqrt{1^2+1^2+(-2)^2}\right)^2 + \left(\frac{a}{6}\sqrt{1^2+1^2+2^2}\right)^2$$

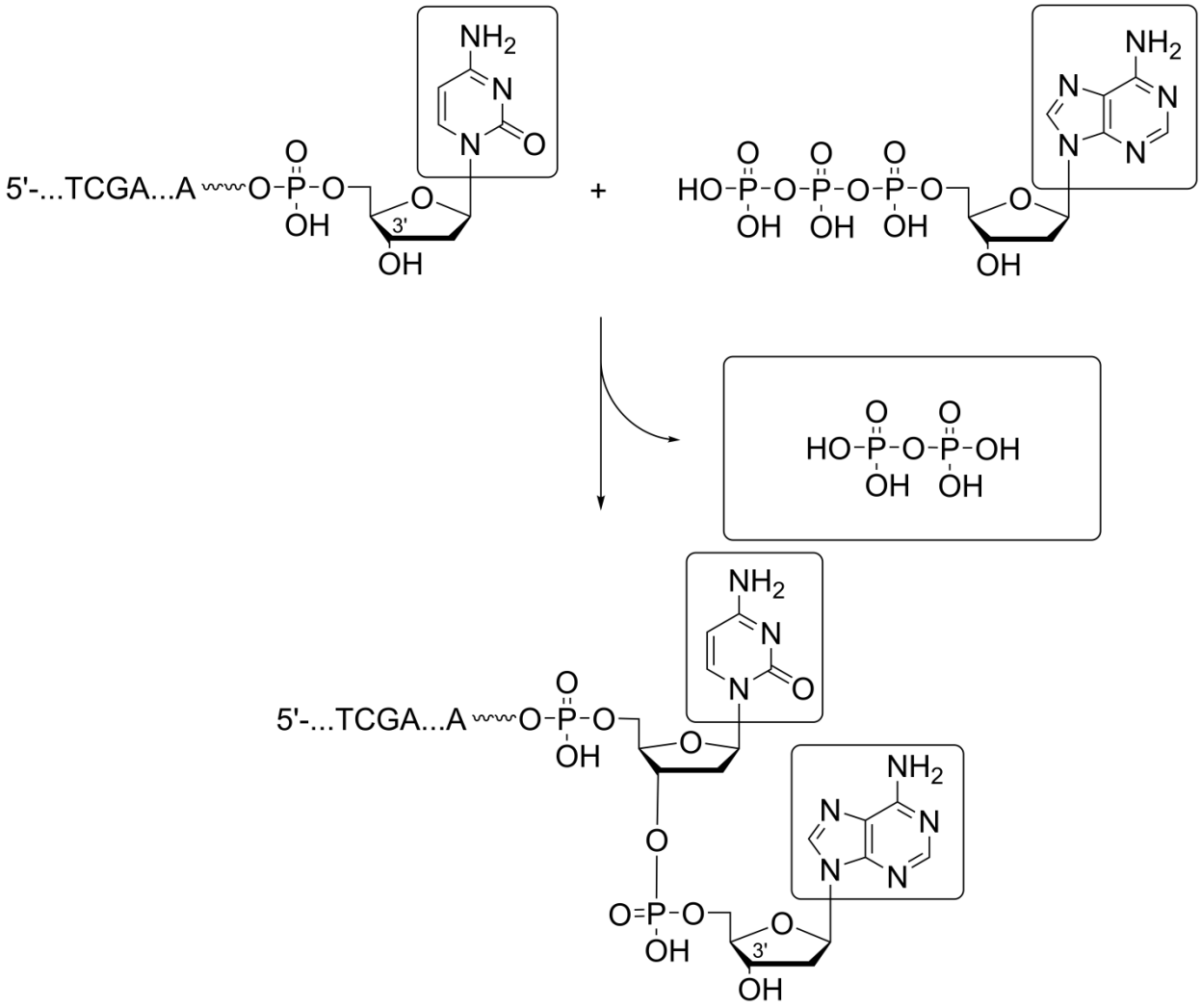
$$\left(\frac{1}{2}\sqrt{1^2+1^2+1^2}\right)^2 + \left(\frac{1}{2}\sqrt{1^2+(-1)^2+(-1)^2}\right)^2 > \left(\sqrt{1^2+0+0}\right)^2$$

All reactions are energetically **favourable**.

Marking note: 1 pt for each missing three dots.
5/3 pt for each correct tick.

DNA sequencing · Solutions

4.1 (5pt)



Marking note: For each correct nitrogenous base: 1 point.
For correct structure of diphosphoric acid: 1 point.

4.2 (5pt)

5'-CGA...ACA**ddT**-3' $\Rightarrow$ [1] is **A**.

Marking note: For correct composition of oligonucleotide: 4 points.
For complementary nitrogenous base: 1 point.

4.3 (5pt)

$(M + 592.42)$ g · mol^{-1} – 5'-CGA...ACA**TddT**-3' $\Rightarrow$ [2] is **A**.

$(M + 881.62)$ g · mol^{-1} – 5'-CGA...ACA**TTddC**-3' $\Rightarrow$ [3] is **G**.

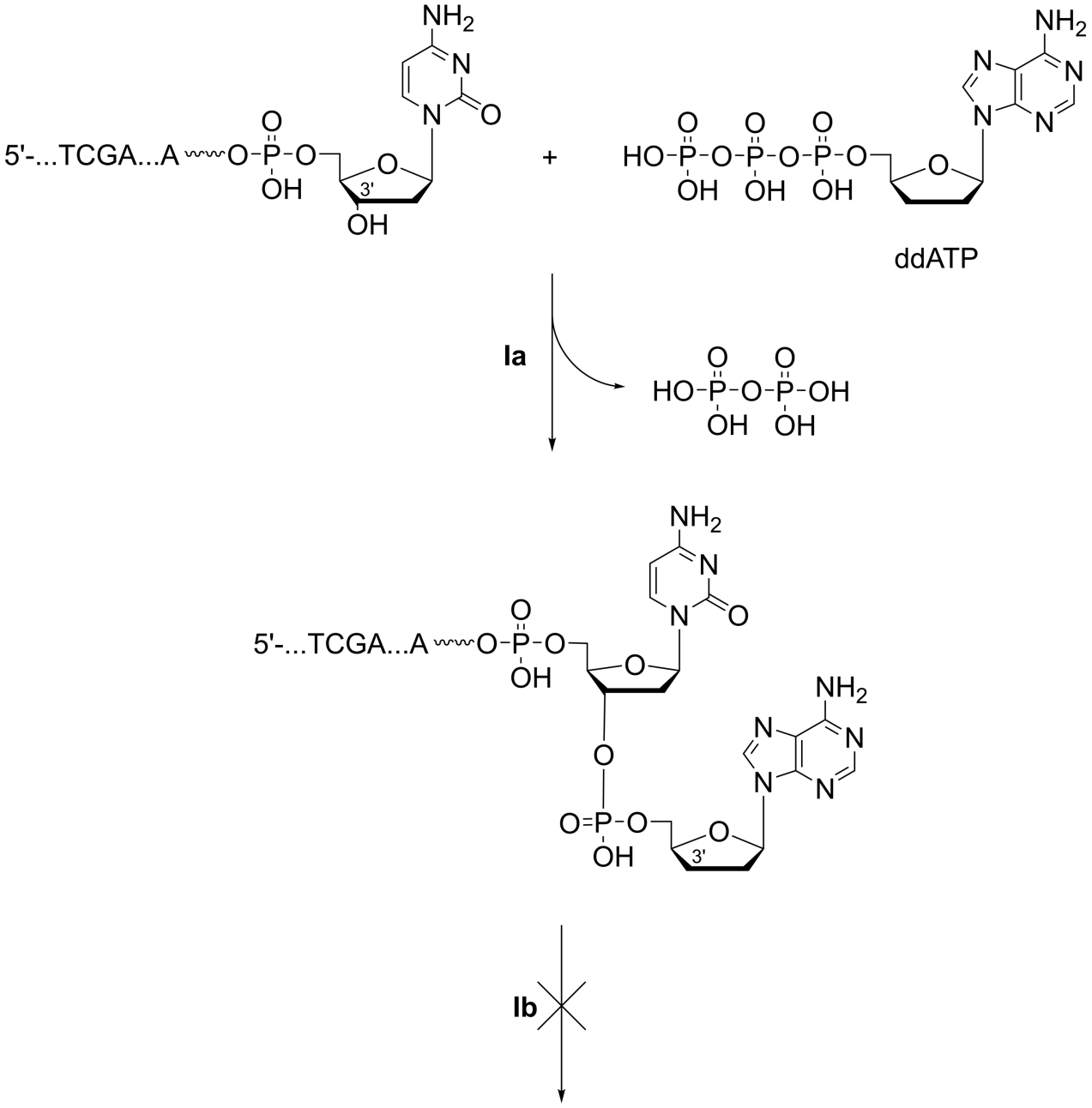
$(M + 1194.84)$ g · mol^{-1} – 5'-CGA...ACA**TTCddA**-3' $\Rightarrow$ [4] is **T**.

$(M + 1524.06)$ g · mol^{-1} – 5'-CGA...ACA**TTCAddG**-3' $\Rightarrow$ [5] is **C**.

Marking note: For correct composition of each oligonucleotide: 1 point.
For each complementary nitrogenous base: 0.25 points.

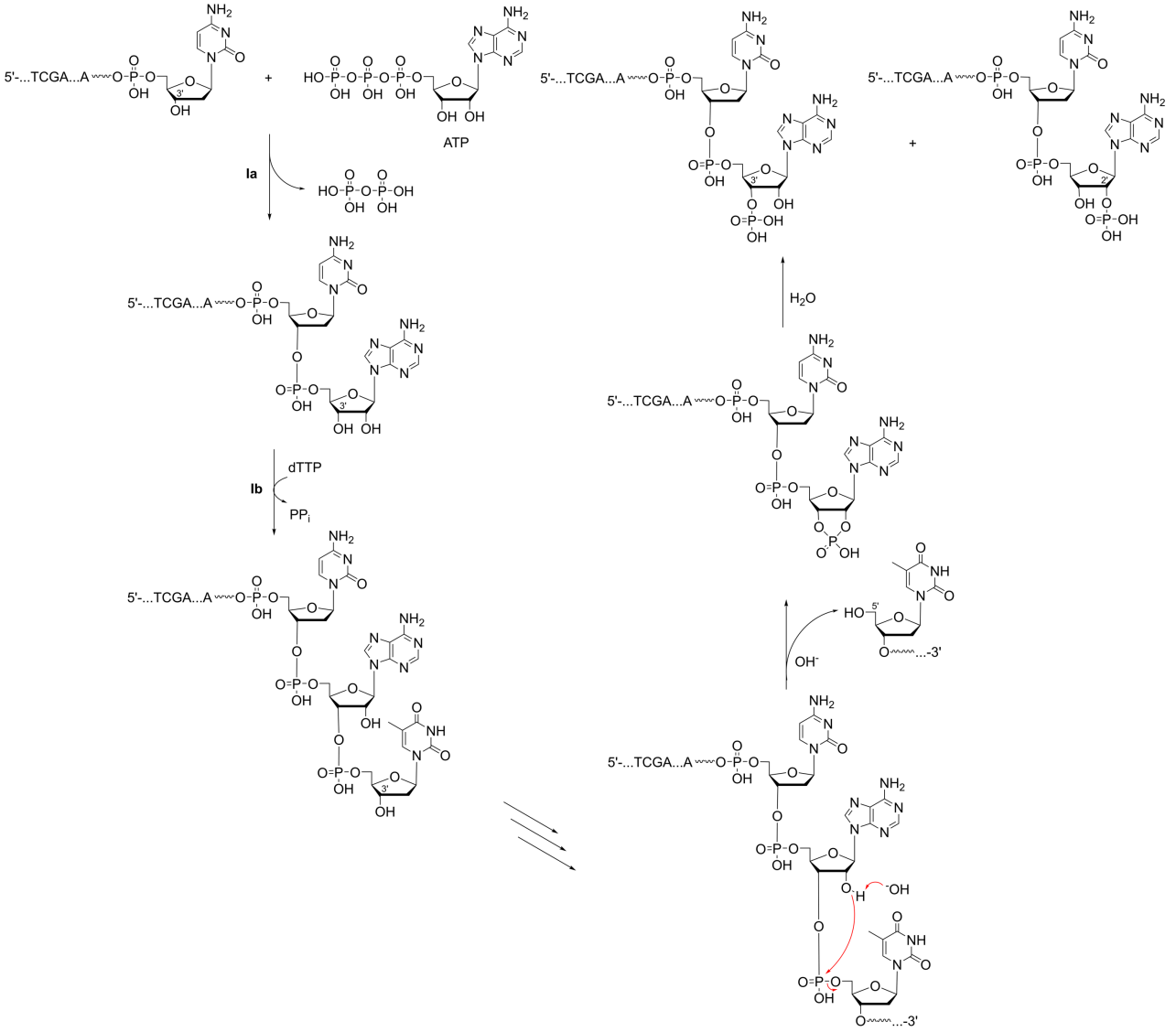
4.4 (6pt)

In case of Sanger's experiment during the growth of the complementary DNA chain ddN without 3'-alcohol group terminates the chain growth at the location of its corresponding dN and forms the oligonucleotides with terminal ddN nitrogenous base and different lengths:



(a) only a full DNA strand complementary to the original DNA strand is formed;
(b) only a small oligonucleotide without a chance to growth is formed due to the absence of one of the dNTPs;
(c) oligonucleotides with different lengths, which indicates the location of the nitrogenous base N, are formed when the concentration of the corresponding dNTP in the reaction mixture is decreased. For example, step Ia cannot continue due to the low concentration of dATP and 5'-CGA...AC-3' can be formed without extending further. This could apply to all strands regardless of their length;

(d) only short oligonucleotides without a chance to growth with ddN as a terminal nucleotide are formed due to the absence of the corresponding dNTPs;
(e) during the growth of the complementary DNA strand N with 2', 3'-diol group is integrated to its corresponding dN and after the alkaline hydrolysis it cleaves off the next base and forms oligonucleotides with terminal N nitrogenous base and different lengths:



Correct answers are (c) and (e).

Marking note: For each correct answer: 3 points.
For each incorrect answer: -2 points penalty.
There is no negative score here.

4.5 (4pt)

$$t_{1/2}(^{32}\mathrm{P}) = 14.3 \text{ days} = 14.3 \times 24 \times 3600 \text{ s} = 1.24 \times 10^{6} \text{ s}$$

$$\lambda(^{32}\mathrm{P}) = \frac{\ln 2}{1.24 \times 10^{6}} = 5.59 \times 10^{-7} \mathrm{s}^{-1}$$

$$A = \lambda \cdot \mathrm{C}(^{32}\mathrm{P}) \rightarrow \mathrm{C}(^{32}\mathrm{P}) = \frac{A}{\lambda} = \frac{10 \times 10^{-3} \times 3.7 \times 10^{10}}{5.59 \times 10^{-7} \times 6.02 \times 10^{23}} = 1.1 \times 10^{-9} \text{ mol} \cdot \mathrm{mL}^{-1}$$

$$\frac{M_{\boldsymbol{R}}}{n_{\mathrm{P32}}} = \frac{0.54 \times 10^{-6}}{1.1 \times 10^{-9}} \approx 491 \text{ g} \cdot \text{mol}^{-1}$$

So, **R** is dATP, only 1 ^{32}P is found in it being located at the α position (unlabelled DNA would be obtained with ^{32}P in different position).

Marking note: For correct lambda(32P) value: 1 point.
For correct C(32P) value: 1 point.
For dATP: 1 point.
For correct location of 32P label: 1 point.

4.6 (10pt)

Possible DNA sequences for each protein end as follows:

Encoded protein	Amino acid sequence	DNA sequence
C-end of **D**	...GlyValMet	5'-...GG?GT?ATGT??...-3'
C-end of **E**	...Glu	5'-...GA?T??...-3'
N-end of **J**	MetSer...	5'-...ATG???...-3'

The C-end of **D** is encoded by the nucleotide residues located at 5'-side of this fragment, while the N-end of **J** by those at 3'-side. At first glance, the minimum amount of nucleotides required to encode only these ends of **D** and **J** is: $3 * (4 + 2) = 18$, which is higher than 17 given in the task. So, encoding is more "dense". This is achieved by shifting the frame of reading and overlapping of the fragments coding different proteins. Thus, one gets for proteins **D**, **E**, and **J**:

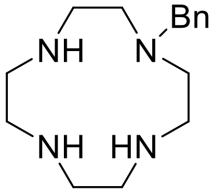
5'-...	?	?	?	?	?	G	?	?	?	?	A	?	?	?	T	C	T	...-3'
	G	G	?	G	T	?	A	T	G	T	?	?						
		G	A	?	T	?	?											
												A	T	G	?	?	?	
									⇓									
5'-...	G	G	A	G	T	G	A	T	G	T	A	A	T	G	T	C	T	...-3'

Marking note: For encoding region of protein D: 2 points.
For encoding region of protein E: 1 point.
For encoding region of protein J: 1 point.
If region encodes proteins D and E together by overlapping: 3 points.
If region encodes proteins D and J together by overlapping: 3 points.

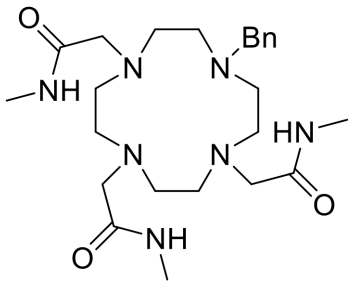
CO_2 detection with a gadolinium complex · Solutions

5.1 (6pt)

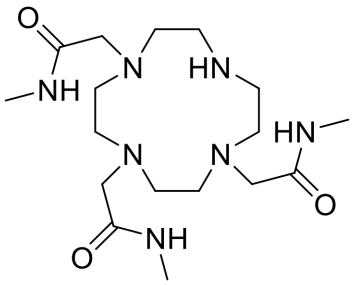
A



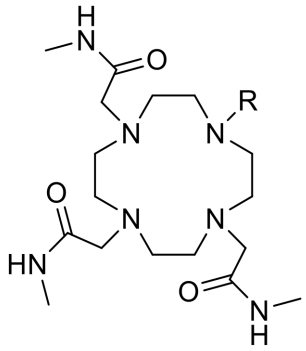
B



C



D



Marking note: Structures A and B - 2 pts each, C and D - 1 pt each.
All N atoms of the macrocycle are equivalent, so any position of the substituent is accepted.
Cyclen without a benzyl group or with more than one benzyl group as A - 0 pts (inconsistent with M(A)).
B with fewer than three amide arms - 0 pts.
Error carried forward: B, C and D receive partial points if they follow correctly and chemically consistently from the student's structure of the previous compound.

5.2 (8pt)

X is a hydrated halide of Gd(III), so it can be written as $GdHal_3 \cdot nH_2O$. As **Y** is a binary anhydrous salt containing Gd^{3+} the most primitive assumption would be **Y** = $GdHal_3$. Since **Y** and **Z** are formed in equimolar ratio, 1 mol of **X** gives 1/2 mol of **Y** and 1/2 mol of **Z**, and each contains one Gd atom. We can define molar masses of unknown compounds as follows:

$$M(Z) = 0.5616 \times M(X)$$

$$\frac{1}{2}M(Z) + \frac{1}{2}M(Y) = 0.6355 \times M(X)$$

$$M(Y) = 0.7094 \times M(X)$$

Both are expressed through Hal and n:

$$M(Y) = 157.25 + 3M(\text{Hal}) \ , \quad M(X) = 157.25 + 3M(\text{Hal}) + 18n$$

$$\frac{M(Y)}{M(X)} = 0.7094 = \frac{157.25 + 3M(\text{Hal})}{157.25 + 3M(\text{Hal}) + 18n}$$

Solving this for $M(\text{Hal})$ and n:

$$45.697 + 0.8718 \times M(\text{Hal}) = 12.769 \times n$$

$$M(\text{Hal}) = 14.6467 \times n - 52.417$$

n must be a whole number, and $M(\text{Hal})$ must be the molar mass of a real anion:

n	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
$M(\text{Hal})$	-37.77	-23.12	-8.48	6.17	20.82	**35.46**	50.11	64.75	79.40	94.05

Only n = 6 gives the mass of a real anion: Cl^- (35.45). For n = 9 the value 79.40 is close to Br (79.90), but the difference of 0.5 g/mol is far larger than the precision of the data (≈ 0.1 g/mol).

$$X = GdCl_3 \cdot 6H_2O \Rightarrow Y = GdCl_3$$

$$M(Z) = 0.5616 \times M(X) = 208.69 \text{ g/mol} \Rightarrow Z = GdOCl$$

X - $GdCl_3 \cdot 6H_2O$	**Y** - $GdCl_3$	**Z** - GdOCl

[1] $2GdCl_3 \cdot 6H_2O \rightarrow GdCl_3 + GdOCl + 2\ HCl + 11H_2O$

[2] $GdCl_3 + H_2O \rightarrow GdOCl + 2\ HCl$

Marking note: Chemicals X, Y, Z - 2 pts each. Balanced equations - 1 pt each.
Correct formulae X, Y, Z without any supporting calculation - 1 pt each.
Any oxide as Y - 0 pts as it is inconsistent with the mass loss on the second stage.
Equations with correct species but not balanced - half of the points.

5.3 (3pt)

Gd^{3+}	[Xe] $4f^7$
N	7
☒ **p**	☐ **d**

Marking note: 1 pt for each correct answer.
Error carried forward: p/d consistent with the student's N receives the point.

5.4 (6pt)

$[\mathrm{D}]_{\mathrm{low}}$

The observed relaxivity R is a weighted average between the 'free' form GdL and the bound complex GdLD, proportional to the fraction of each form:

$$R = R_{\mathrm{GdL}}\left(\frac{[\mathrm{GdL}]}{[\mathrm{GdL}]_0}\right) + R_{\mathrm{GdLD}}\left(\frac{[\mathrm{GdLD}]}{[\mathrm{GdL}]_0}\right)$$

$$[\mathrm{GdL}]_0 = [\mathrm{GdL}] + [\mathrm{GdLD}]$$

$$[\mathrm{D}]_0 = [\mathrm{D}] + [\mathrm{GdLD}]$$

According to equilibrium:

$$[\mathrm{GdLD}] \approx [\mathrm{D}]_0 \quad \text{when} \quad [\mathrm{D}]_0 < [\mathrm{GdL}]_0$$

At very low concentrations of $[\mathrm{D}]_0 \Rightarrow [\mathrm{D}]_0 \to 0$:

$$R = R_{\mathrm{GdL}}\left(\frac{[\mathrm{GdL}]}{[\mathrm{GdL}]_0}\right) + R_{\mathrm{GdLD}}\left(\frac{[\mathrm{D}]_0}{[\mathrm{GdL}]_0}\right)$$

$$R_{\mathrm{GdLD}}\left(\frac{[\mathrm{D}]_0}{[\mathrm{GdL}]_0}\right) \to 0 \ ; \quad [\mathrm{GdL}] \approx [\mathrm{GdL}]_0 \quad \text{as} \quad [\mathrm{D}]_0 \to 0$$

$$R \approx R_{\mathrm{GdL}}\left(\frac{[\mathrm{GdL}]_0}{[\mathrm{GdL}]_0}\right) \Rightarrow R \approx R_{\mathrm{GdL}}$$

Answer: $R = R_{\mathrm{GdL}}$

$[\mathrm{D}]_{\mathrm{high}}$

According to equilibrium:

$$[\mathrm{GdLD}] \approx [\mathrm{GdL}]_0 \quad \text{when} \quad [\mathrm{D}]_0 > [\mathrm{GdL}]_0$$

At very high concentrations of $[\mathrm{D}]_0 \Rightarrow [\mathrm{D}]_0 \to \infty$:

$$R = R_{\mathrm{GdL}}\left(\frac{[\mathrm{GdL}]}{[\mathrm{GdL}]_0}\right) + R_{\mathrm{GdLD}}\left(\frac{[\mathrm{GdL}]_0}{[\mathrm{GdL}]_0}\right)$$

$$[\mathrm{GdL}] \to 0 \quad \text{as} \quad [\mathrm{GdLD}] \approx [\mathrm{GdL}]_0 \ ; \quad R_{\mathrm{GdL}}\left(\frac{[\mathrm{GdL}]}{[\mathrm{GdL}]_0}\right) \to 0$$

$$R \approx R_{\mathrm{GdLD}}\left(\frac{[\mathrm{GdL}]_0}{[\mathrm{GdL}]_0}\right) \Rightarrow R \approx R_{\mathrm{GdLD}}$$

Answer: $R = R_{\mathrm{GdLD}}$

Marking note: [D]low: 3 pts in total
[D]low: any correct answer without any supporting explanation - 1 pt
[D]low: for approximation [GdLD] ≈ [D]0 - 1 pt
[D]low: derivation of equation when [D]0 -> 0 - 1 pt
[D]high: 3 pts in total
[D]high: any correct answer without any supporting explanation - 1 pt

[D]high: for approximation [GdLD] ≈ [GdL]0 - 1 pt
[D]high: derivation of equation when [D]0 -> infinity - 1 pt

5.5 (9pt)

At $[\mathrm{D}]_0 = 0$ mM, from the previous question:

$$R = R_{\mathrm{GdL}} = 6.392 \mathrm{mM}^{-1}\mathrm{s}^{-1}$$

At $[\mathrm{D}]_0 = 10$ mM, from the previous question as well:

$$R = R_{\mathrm{GdLD}} = 3.240 \mathrm{mM}^{-1}\mathrm{s}^{-1}$$

By mass conservation (mass balance):

$$[\mathrm{GdL}] = [\mathrm{GdL}]_0 - [\mathrm{GdLD}], \quad [\mathrm{D}] = [\mathrm{D}]_0 - [\mathrm{GdLD}]$$

Substituting into K_a:

$$K_a = \frac{[\mathrm{GdLD}]}{([\mathrm{GdL}]_0 - [\mathrm{GdLD}]) \times ([\mathrm{D}]_0 - [\mathrm{GdLD}])}$$

$$R = R_{\mathrm{GdL}}\left(1 - \frac{[\mathrm{GdLD}]}{[\mathrm{GdL}]_0}\right) + R_{\mathrm{GdLD}}\left(\frac{[\mathrm{GdLD}]}{[\mathrm{GdL}]_0}\right)$$

From the last equation:

$$\alpha_{\mathrm{GdLD}} = \frac{[\mathrm{GdLD}]}{[\mathrm{GdL}]_0} = \frac{R - R_{\mathrm{GdL}}}{R_{\mathrm{GdLD}} - R_{\mathrm{GdL}}}$$

Substituting into K_a:

$$K_a = \frac{\alpha_{\mathrm{GdLD}}[\mathrm{GdL}]_0}{([\mathrm{GdL}]_0 - \alpha_{\mathrm{GdLD}}[\mathrm{GdL}]_0) \times ([\mathrm{D}]_0 - \alpha_{\mathrm{GdLD}}[\mathrm{GdL}]_0)}$$

$$\alpha_{\mathrm{GdLD}} = \frac{R - R_{\mathrm{GdL}}}{R_{\mathrm{GdLD}} - R_{\mathrm{GdL}}}$$

Taking any point from the data and using these two equations leads to final K_a value:

$\frac{[\mathrm{D}]_0}{\mathrm{mM}}$	**0.050**	**0.10**	**0.300**	**0.500**	**0.55**	**3.0**	**5.0**
$\frac{R}{\mathrm{mM}^{-1}\mathrm{s}^{-1}}$	6.099	5.811	4.740	3.966	3.843	3.283	3.264
α_{GdLD}	0.092957	0.184327	0.5241116	0.76967	0.808693	0.986358	0.99238
$\frac{K_a}{\mathrm{M}^{-1}}$	29102.25	28837.04	29027.26	29015.73	29022.30	28842.52	28938.53

$R_{\mathrm{GdL}} = 6.392 \mathrm{mM}^{-1}\mathrm{s}^{-1}$	$R_{\mathrm{GdLD}} = 3.240 \mathrm{mM}^{-1}\mathrm{s}^{-1}$	$K_a = 2.90 \times 10^4 \mathrm{M}^{-1}$

Marking note: 3 pts for each correct value (R_GdL, R_GdLD, Ka).
2 pts if the method is correct but there is an arithmetic error.
Any correct value without calculations - 0 pts.
Partial credit may be given for any reasonable statement or equation.

5.6 (3pt)

$R = 3.5 \mathrm{mM}^{-1}\mathrm{s}^{-1}$, $[\mathrm{GdL}]_0 = 500 \times 10^{-6}$ M:

$$K_a = \frac{\alpha_{\mathrm{GdLD}}[\mathrm{GdL}]_0}{([\mathrm{GdL}]_0 - \alpha_{\mathrm{GdLD}}[\mathrm{GdL}]_0)([\mathrm{D}]_0 - \alpha_{\mathrm{GdLD}}[\mathrm{GdL}]_0)}$$

$$R = R_{\mathrm{GdL}}\left(1 - \frac{[\mathrm{GdLD}]}{[\mathrm{GdL}]_0}\right) + R_{\mathrm{GdLD}}\left(\frac{[\mathrm{GdLD}]}{[\mathrm{GdL}]_0}\right)$$

$$[\mathrm{GdLD}] = 458.7\ \mu\mathrm{M} \Rightarrow [\mathrm{D}]_0 = 842.3\ \mu\mathrm{M}$$

If given values $K_a = 3.0 \times 10^5 \mathrm{M}^{-1}$; $R_{\mathrm{GdL}} = 6.01 \mathrm{mM}^{-1}\mathrm{s}^{-1}$; $R_{\mathrm{GdLD}} = 2.74 \mathrm{mM}^{-1}\mathrm{s}^{-1}$ *are used:*

$$\alpha_{\mathrm{GdLD}_1} = 0.7676 \Rightarrow [\mathrm{D}]_0 = 394.8\ \mu\mathrm{M}$$

Answer: *[HCO_3^-] = 842.3 μM (394.8 μM if given values used)*

Marking note: 3 pts for the correct result. Full marks are also awarded if the student uses their own values from Q.5 or the values given in the problem statement.
2 pts if the method is correct but there is an arithmetic error.
1 pt for the correct answer without supporting calculations.
0 pts for an incorrect approach.

5.7 (1pt)

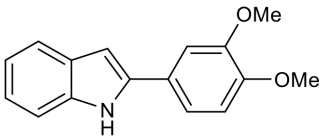
☐ A	☒ **B**	☐ C	☐ D	☐ E

Marking note: 1 pt for correct answer (B).
–0.5 pt for each incorrect answer selected.
0 pt for any other answers.

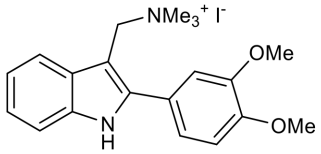
Strychnine · Solutions

6.1 (24pt)

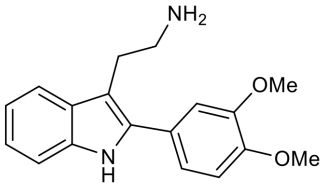
A



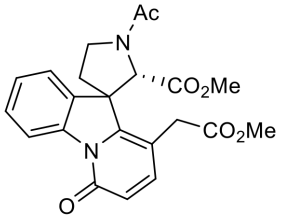
B



C

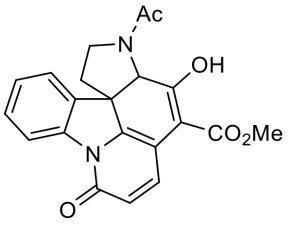


F

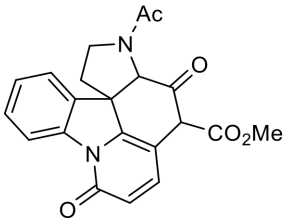


F with Et/Me esters is accepted for partial credit.

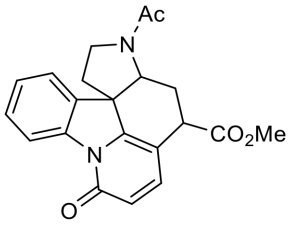
G



or



I

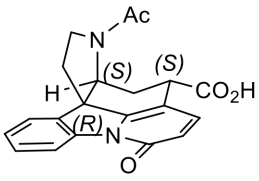


Marking note: A: 4 pt
B: 4 pt
C: 4 pt
F: 4 pt; F with Et/Me esters accepted for partial credit: 2 pt
G: 4 pt (either the enol or the keto form)
I: 4 pt

6.2 (6pt)

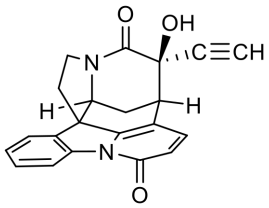
1-b, **2**-g, **3**-e

6.3 (6pt)

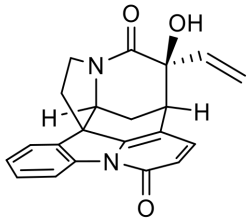


6.4 (30pt)

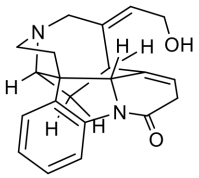
L



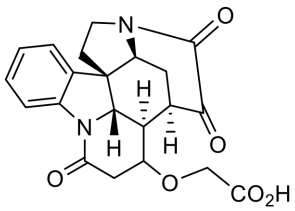
M



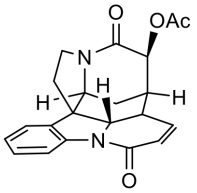
O



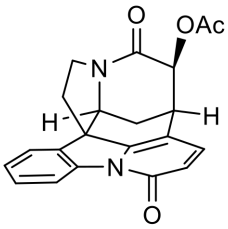
P



R

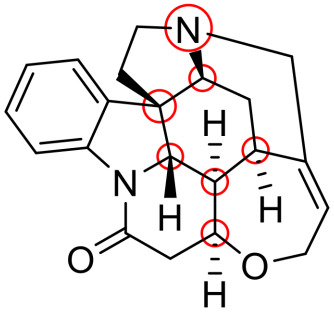


S



Marking note: L: 4 pt; 2 pt for incorrect diastereomer
M: 4 pt
O: 6 pt
P: 6 pt
R: 6 pt
S: 4 pt

6.5 (7pt)



Marking note: Each correct circled atom: 1 pt

Pb means Problem · Solutions

7.1 (2pt)

$$\mathrm{Pb(OH)_{2(s)} \rightleftharpoons Pb(OH)_{2(aq)}}$$

$$K_1 = \left[\mathrm{Pb(OH)_{2(aq)}}\right] = \beta_2 K_s = 1.738 \times 10^{-5}$$

Marking note: 1 pt for derivation
1 pt for correct value
2 pts in total

7.2 (5pt)

a)

$$[\mathrm{Pb^{2+}}] = \frac{K_s}{[\mathrm{OH^-}]^2}$$

$$[\mathrm{PbOH^+}] = \beta_1 [\mathrm{Pb^{2+}}][\mathrm{OH^-}] = \frac{K_s \beta_1}{[\mathrm{OH^-}]} = \frac{K_s \beta_1 [\mathrm{H^+}]}{K_w}$$

$$\left[\mathrm{Pb(OH)_{2(aq)}}\right] = \beta_2 K_s \tag{1}$$

$$[\mathrm{Pb(OH)_3^-}] = \beta_3 [\mathrm{Pb^{2+}}][\mathrm{OH^-}]^3 = \beta_3 K_s [\mathrm{OH^-}] = \frac{K_s \beta_3 K_w}{[\mathrm{H^+}]}$$

b)

$$s = \left[\mathrm{Pb^{2+}_{(aq)}}\right] + \left[\mathrm{PbOH^+_{(aq)}}\right] + \left[\mathrm{Pb(OH)_{2(aq)}}\right] + \left[\mathrm{Pb(OH)^-_{3(aq)}}\right]$$

$$s = \frac{K_s [\mathrm{H^+}]^2}{K_w^2} + \frac{K_s \beta_1 [\mathrm{H^+}]}{K_w} + \beta_2 K_s + \frac{\beta_3 K_s K_w}{[\mathrm{H^+}]} \tag{2}$$

Marking note: a) 1 pt for [Pb2+]=K_s/[OH^-]^2
a) 1 pt for [PbOH+] = beta1 Ks [H+]/Kw
a) 1 pt for [Pb(OH)2(aq)] = beta2 Ks
a) 1 pt for [Pb(OH)3-] = beta3 Ks Kw/[H+]
b) 1 pt for the expression of s
5 pts in total

7.3 (2pt)

a) pH = 6.5

$s = 1.1$ M

b) pH = 8.5

$s = 5.57 \times 10^{-3}$ M

Answers with provided equation:

pH = 6.5: $s = 1.1$ M

pH = 8.5: $s = 5.56 \times 10^{-3}$ M

Marking note: a) 1 pt for s = 1.1 M at pH 6.5
b) 1 pt for s = 5.57 x 10^-3 M at pH 8.5 (5.56 x 10^-3 M with the provided equation)
2 pts in total

7.4 (2pt)

a) $\mathrm{Pb^{2+}} + \mathrm{L} \rightleftarrows [\mathrm{PbL}]^{2+}$

b) $[\mathrm{PbL}]^{2+} + \mathrm{H_2Y^{2-}} \rightleftarrows \mathrm{PbY^{2-}} + \mathrm{L} + 2\mathrm{H^+}$

Marking note: a) 1 pt
b) 1 pt
2 pts in total

7.5 (1pt)

$$K_d(\mathrm{PbL}) > K_d(\mathrm{PbY^{2-}})$$

Marking note: 1 pt

7.6 (4pt)

$$[\mathrm{PbL}]^{2+} + \mathrm{H_2Y^{2-}} \rightleftarrows \mathrm{PbY^{2-}} + \mathrm{L} + 2\mathrm{H^+} \quad \Delta G^\circ{}_1 = 50.77\ \mathrm{kJ/mol}, \quad K_1 = 1.26 \times 10^{-9}$$

$$\mathrm{PbY^{2-}} \rightleftarrows \mathrm{Pb^{2+}} + \mathrm{Y^{4-}} \quad K_{d1} = 1 \times 10^{-18}$$

We are asked to calculate:

$$[\mathrm{PbL}]^{2+} \rightleftarrows \mathrm{Pb^{2+}} + \mathrm{L} \quad K_{d2} = ?$$

We need one more reaction to calculate the unknown value:

$$\mathrm{H_2Y^{2-}} \rightleftarrows 2\mathrm{H^+} + \mathrm{Y^{2-}}$$

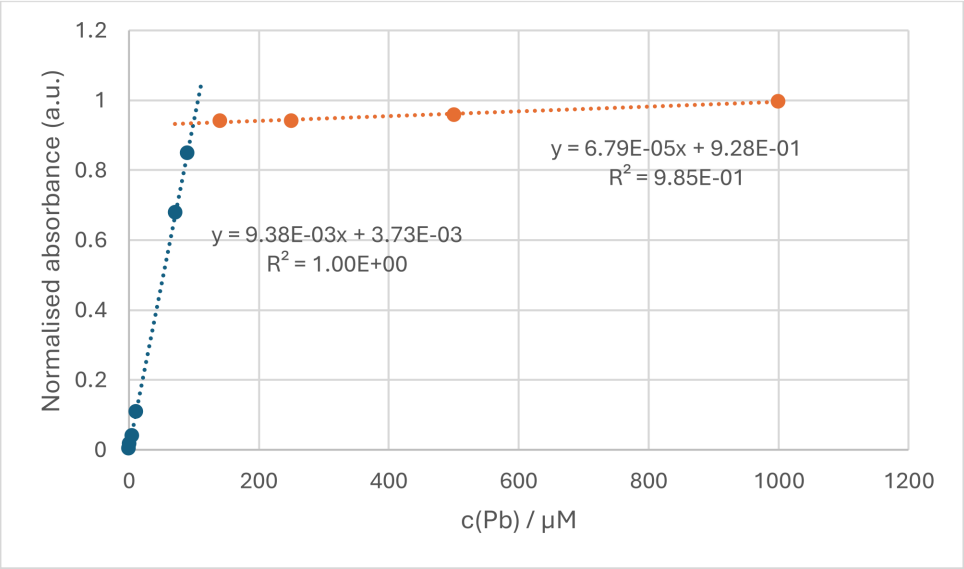
$$K_2 = K_{a3}K_{a4} = 3.81 \times 10^{-17}$$

Then,

$$K_d(\mathrm{PbL}) = \frac{K_1 \times K_{d1}}{K_2} = 3.31 \times 10^{-11}$$

Marking note: 4 pts in total

7.7 (4pt)



a) After plotting the graph, we can see that absorbance reaches its maximum in the region between 90 and 140 μM, then remains almost stable with some slight changes. It means that the complex is fully formed in this region (saturated). The only combination that fits this data is Pb:L = 1:1.

b) As we see from the graph, there are 2 regions: 0-90.50 μM and 140.78-1000 μM which form straight lines with equations: $y = 0.00938x + 0.0037$ and $y = 6.79 \times 10^{-5}x + 0.928$, respectively. The cross-section of the lines will give the saturation point.

$$0.00938x + 0.0037 = 6.79 \times 10^{-5}x + 0.928$$

$$\boldsymbol{x = 99.26\ \mu M}$$

Marking note: a) 1 pt for Pb:L = 1:1
b) 3 pt for the saturation point x = 99.26 uM from the intersection of the two lines
4 pts in total

eXotic · Solutions

8.1 (7pt)

Reaction of element **X** with fluorine gives binary compounds. Then, **A**, **B**, and **C** are fluorides XF_a, XF_b, XF_c respectively. Hydrolysis of **A** produces mixture 1 with $M(\text{mixture 1}) = 49.10 \times 2 = 98.20$ g/mol

It is said that the mixture consists of simple compounds, meaning the hydrolysis proceeds with a redox reaction. As the oxidation of fluorine atoms is likely impossible due to their high electronegativity, the mixture being formed during hydrolysis is most likely **X** and oxygen:

$$XF_a + \frac{a}{2}H_2O = X + \frac{a}{4}O_2 + a\ HF$$

Using the suggested reaction equation and molar mass of mixture 1:

$$\frac{X + 8a}{\frac{a}{4} + 1} = 98.20; \quad X = 16.55a + 98.20$$

a	X	
1	114.75	In
2	**131.3**	**Xe**
3	147.85	-
4	164.4	-
5	180.95	Ta

The only fitting value of *a* is *a* = 2, considering the properties of **X**. Then **A** - XeF_2.

For xenon, there are three fluorides that are formed when it reacts with fluorine: XeF_2, XeF_4, XeF_6. **C** does not produce any gas upon reaction with water, meaning there is no redox reaction and the oxidation state of **X** in **D** is the same as in **C**. That gives us a hint that hydrolysis of **B** is not just a redox reaction, it is a disproportionation reaction with formation of **D** (in the form of oxide/hydroxide) and mixture 2 (same composition as mixture 1). Knowing the tendency of XeF_4 to disproportionate during hydrolysis, we can propose that: **B** - XeF_4, **C** - XeF_6. Then,

$$XeF_6 + 3H_2O \rightarrow XeO_3 + 6HF$$

$$6XeF_4 + 12H_2O \rightarrow 2XeO_3 + 4Xe + 3O_2 + 24HF$$

We can prove proposed compounds by calculating the molar mass of the mixture 2:

$$M(\text{mixture}) = \frac{131.30 \times 4 + 32 \times 3}{7} = 88.74 = 44.37 \times 2$$

That fits the problem condition.

X - Xe	**A** - XeF_2	**B** - XeF_4
C - XeF_6	**D** - XeO_3	**E** - XeO_2

Marking note: A - XeF2: 2 pt (1 pt for calculations, 1 pt for correct compound B)
1 pt for each compound
7 pt in total

8.2 (4pt)

SbF_5 is a very strong Lewis acid and forms fluoro complexes when it reacts with other compounds (like XeF_2). **F** is obtained from XeF_2 and SbF_5 in a ratio of 1:2, then the formula of **F** is $XeSb_2F_{12}$. Bearing in mind that this substance contains fluorine in the cation and in the anion, the oxidation number of xenon and antimony, the final formula of **G** is $[XeF]^+[Sb_2F_{11}]^-$. **G** contains a bond Xe-Xe (one of the longest), then **G** must contain at least two xenons. Then the molar mass of **G**:

$$M_H = \frac{131.3 \cdot 2}{0.2286} = 1148.73 \text{ g/mol}$$

and fluorine content:

$$N_F = \frac{1148.73 \times 0.3474}{19} = 21$$

the remainder of the mass: $\Delta M = 487.13$ g/mol corresponds to four antimony atoms: $\frac{4871.13}{121.75} = 4$. So, the formula **G** - $[Xe_2]^+[Sb_4F_{21}]^-$

Formation compound of **G**:

$$3Xe + [XeF]^+[Sb_2F_{11}]^- + 6SbF_5 \rightarrow 2[Xe_2]^+[Sb_4F_{21}]^-$$

Formation compound of **F**:

$$XeF_2 + 2SbF_5 \rightarrow [XeF]^+[Sb_2F_{11}]^-$$

G - $[Xe_2]^+[Sb_4F_{21}]^-$	**F** - $[XeF]^+[Sb_2F_{11}]^-$

Marking note: 1 pt for each compound
1 pt for each reaction
4 pts in total

8.3 (8pt)

H is a binary compound containing a d-metal and non-metal. As we are dealing with fluorides in each reaction, the non-metal is most likely fluorine. Each bridging ligand corresponds to 2 central atoms, meaning the empirical formula for **H** is $MeF_{2+\frac{1}{2}\cdot 2}$ or MeF_3.

Then, according to the condition of the problem, Xe and **H** reaction 6:1, **I** and **G** are obtained in the same amount, **I** and **J** contain a d-metal in the oxidation state of +2, and **I** contains $Sb_2F_{11}^-$. The general equation is:

$$MeF_3 + 6Xe + 8SbF_5 \rightarrow [MeXe_4]^{2+}[Sb_2F_{11}]_2^- + [Xe_2]^+[Sb_4F_{21}]^-$$

and decompositions of **I**:

$$[MeXe_4]^{2+}[Sb_2F_{11}]_2^- \rightarrow 4Xe\uparrow + SbF_5 + \boldsymbol{J}$$

Then from the mass loss we determine Me:

$$0.3228 = \frac{4 \times 131.30}{Me + 1430.2}; \quad Me = 196.8 \text{ g/mol is Au}$$

As oxidation state of gold is the same in **I** and **J** and is equal to +2, the salt **J** is $Au(SbF_6)_2$

Reaction formation compound of **I**:

$$AuF_3 + 6Xe + 8SbF_5 \rightarrow [AuXe_4]^{2+}[Sb_2F_{11}]_2^- + [Xe_2]^+[Sb_4F_{21}]^-$$

Reaction decompositions of **I**:

$$[AuXe_4]^{2+}[Sb_2F_{11}]_2^- \rightarrow Au(SbF_6)_2 + 2SbF_5 + 4Xe$$

H - AuF_3	**I** - $[AuXe_4]^{2+}[Sb_2F_{11}]_2^-$	**J** - $Au(SbF_6)_2$

Marking note: 2 pts for each compound
1 pt for each reaction
8 pts in total