

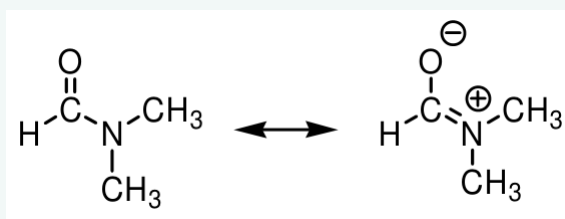
IChO 2005

Theory problems and solutions · Taipei, Taiwan · 8 theory problems with complete solutions

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Problem 1: Chemistry of Amides and Phenols

Condensation of a carboxylic acid with an amine gives an amide product. For example, condensation of formic acid with dimethylamine forms N,N-dimethylformamide (DMF), which can be described as the following resonance structures.



1.1 Predict the order of melting points among N,N-dimethylformamide (compound **A**), N-methylacetamide ($\text{CH}_3\text{CONHCH}_3$, compound **B**), and propionamide (compound **C**, $\text{CH}_3\text{CH}_2\text{CONH}_2$). Express your answer from high to low melting point as follows:

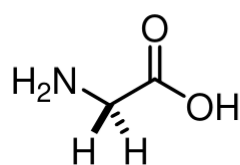
____ > ____ > ____ (Insert compound codes **A**, **B**, **C**)

1.2 Carbonyl groups are usually identified by their characteristic strong absorptions in the infrared spectra. The position of the absorption is dependent on the strength of the $\text{C}=\text{O}$ bond, which in turn is reflected in their bond lengths. In amides, the strength of the carbonyl groups can be shown by the resonance structure noted above. For example, cyclohexanone shows an absorption at 1715 cm^{-1} for the carbonyl group ($\text{C}=\text{O}$). In comparison with cyclohexanone, predict the absorption band for the carbonyl group in propionamide. Select your answer from the following choices.

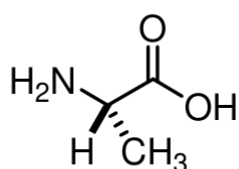
- (a) 1660 cm^{-1} because of the shorter carbonyl bond length.
- (b) 1660 cm^{-1} because of the longer carbonyl bond length.
- (c) 1740 cm^{-1} because of the shorter carbonyl bond length.
- (d) 1740 cm^{-1} because of the longer carbonyl bond length.

1.3 Glycine ($\text{H}_2\text{N}-\text{CH}_2-\text{COOH}$) is an α -amino acid. Three glycine molecules can form a tripeptide Gly-Gly-Gly via amide linkages, accompanied by elimination of two water molecules. Draw the structural formula of this tripeptide.

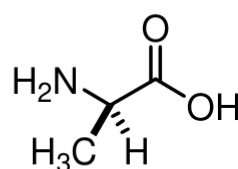
1.4 When an α -amino acid contains a substituent, there is a possibility of optical isomers. For example, L-alanine and D-alanine are two enantiomers. What is the number of all possible linear tripeptides that can be formed from the following three amino acids: glycine, L-alanine and D-alanine as the starting materials in the condensation reaction?



Glycine (Gly)



L-Alanine (L-Ala)



D-Alanine (D-Ala)

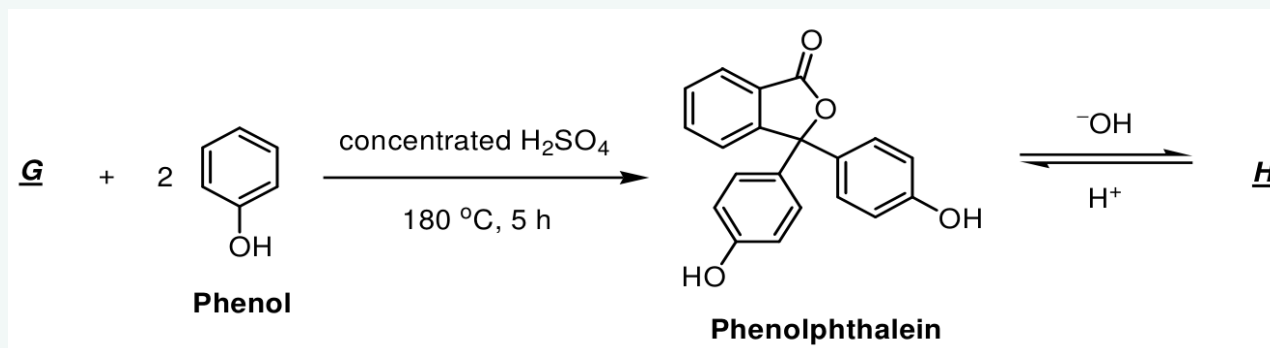
1.5 Among the tripeptides synthesized in 1-4, how many are optically active?

Nowadays, polyacrylamide gel associated with electrophoresis (PAGE) was widely used in analyses of proteins and nucleic acids. However, one of the first applications of polyamide gel is the separation of phenol compounds on thin-layer chromatography. The phenol compounds bearing different substituents have varied acidities. The higher acidity results in stronger binding to PAGE gel.

1.6 Predict the binding affinity of phenol (compound **D**), 4-methylphenol (compound **E**) and 4-nitrophenol (compound **F**) with a polyamide gel. Express your answer from high to low binding affinity as follows:

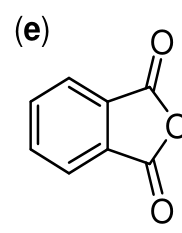
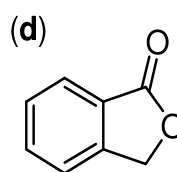
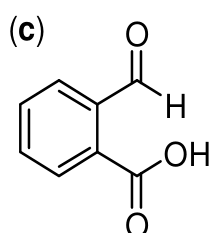
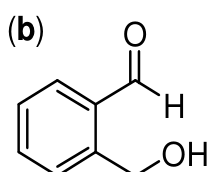
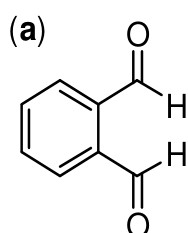
____ > ____ > ____ (Insert compound codes **D**, **E**, and **F**)

The absorption maximum of a molecule in its ultraviolet and visible spectrum (UV-vis spectrum) is related to the number of conjugated double bonds in a chain. A compound containing more than 5 conjugated double bonds tends to absorb visible light, and hence shows the complementary colour. For example, phenolphthalein is a commonly used acid-base indicator, which is colourless in acidic and neutral solutions, but reddish pink in basic solutions (*pH* 8.3–10.0).



1.7 Draw the structural formula of **H** derived from phenolphthalein that is attributable to the reddish pink colour in aqueous NaOH solution.

1.8 A simple way to prepare phenolphthalein is via condensation of compound **G** with 2 equivalents of phenol. What is the most effective reagent for **G** to accomplish this transformation? Select your answer from the following compounds.

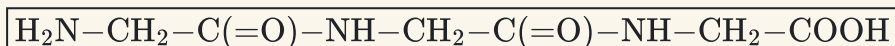


Answers

- 1.1 $C > B > A$: propionamide CCC(=O)N > N-methylacetamide CC(=O)NC > N,N-dimethylformamide CN(C)C=O.

- 1.2 (b): 1660 cm^{-1} , because the carbonyl bond is longer.

- 1.3 **Glycylglycylglycine (triglycine)**, NCC(=O)NCC(=O)NCC(=O)O:



- 1.4 27 linear tripeptides.
- 1.5 26 optically active tripeptides, comprising 13 enantiomeric pairs.
- 1.6 $F > D > E$: 4-nitrophenol Oc1ccc([N+](=O)[O-])cc1 > phenol Oc1ccccc1 > 4-methylphenol (p-cresol) Cc1ccc(O)cc1.
- 1.7 **H is the ring-opened quinonoid dianion of phenolphthalein**, $\text{C}_{20}\text{H}_{12}\text{O}_4^{2-}$. One resonance contributor is O=C([O-])c1ccccc1C(=C1C=CC(=O)C=C1)c1ccc([O-])cc1.
- 1.8 (e): **G is phthalic anhydride**, O=C1OC(=O)c2ccccc21.

Solution

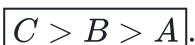
1.1

These three amides are constitutional isomers with the same molecular formula, $\text{C}_3\text{H}_7\text{NO}$. Their different capacities for intermolecular hydrogen bonding provide the principal basis for the prediction.

Compound	Amide type	Number of N–H bonds per molecule
A, N,N-dimethylformamide	Tertiary	0
B, N-methylacetamide	Secondary	1
C, propionamide	Primary	2

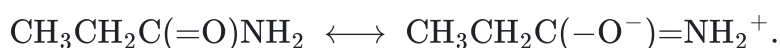
All three have a carbonyl oxygen that can accept hydrogen bonds. Propionamide has two hydrogen-bond donor hydrogens and can form an extensive intermolecular network. N-methylacetamide has one, whereas N,N-dimethylformamide has none.

The expected strength of the hydrogen-bonded crystal lattice therefore increases from A to B to C, giving



1.2

The nitrogen lone pair in propionamide is delocalized into the carbonyl group:



The charge-separated resonance contributor of propionamide has SMILES CCC([O-])=[NH2+].

This contribution gives the carbonyl bond some single-bond character. Consequently, compared with the carbonyl bond in cyclohexanone, O=C1CCCCC1, the amide carbonyl bond is longer and has a smaller stretching force constant.

In the harmonic-oscillator approximation,

$$\tilde{\nu} \approx \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}},$$

where k is the force constant and μ is the effective reduced mass. The smaller force constant lowers the absorption wavenumber relative to 1715 cm^{-1} .

Thus the correct choice is

(b): 1660 cm^{-1} , because of the longer carbonyl bond length.

1.3

Glycine is NCC(=O)O. Joining three glycine molecules requires two peptide bonds, each formed with elimination of one water molecule, O:



The product is **glycylglycylglycine**, also called **triglycine**, NCC(=O)NCC(=O)NCC(=O)O.

The requested drawing is a linear chain with a free amino group at one end, a free carboxyl group at the other, and two intervening -C(=O)-NH- peptide linkages. Each amino-acid residue has a CH_2 group at its α -carbon.

1.4

The available residues are:

Amino acid	Configuration	SMILES
Glycine	Achiral	<chem>NCC(=O)O</chem>
L-alanine	<i>S</i>	<chem>N[C@@H](C)C(=O)O</chem>
D-alanine	<i>R</i>	<chem>N[C@H](C)C(=O)O</chem>

Each of the three positions can independently contain any of these three residues. Repetition is allowed, as illustrated by Gly-Gly-Gly in 1.3.

Peptide sequences are read from the amino terminus to the carboxyl terminus. Because these termini are different, reversing a sequence generally gives a different peptide.

Therefore,

$$N = 3 \times 3 \times 3 = \boxed{27}.$$

1.5

Gly-Gly-Gly contains no stereogenic centre and is achiral. Every other peptide contains at least one alanine residue.

Taking a mirror image exchanges L-alanine and D-alanine at each occupied position while leaving glycine unchanged. The distinct amino and carboxyl termini prevent a symmetry operation from reversing the chain and identifying different residue positions. Thus mixed L/D sequences do not

produce meso peptides.

Only Gly-Gly-Gly is identical to its mirror image. Hence,

$$N_{\text{optically active}} = 27 - 1 = \boxed{26}.$$

These constitute

$$\frac{26}{2} = \boxed{13}$$

enantiomeric pairs. This counts individual peptide species; an equimolar mixture of an enantiomeric pair would have zero net optical rotation.

1.6

The problem states that greater phenol acidity gives stronger binding to the gel. The acidity order follows from stabilization of the conjugate bases:

Parent compound	Conjugate base	SMILES of conjugate base
D, phenol	Phenoxide	<chem>[O-]c1ccccc1</chem>
E, 4-methylphenol	4-Methylphenoxide	<chem>Cc1ccc([O-])cc1</chem>
F, 4-nitrophenol	4-Nitrophenoxide	<chem>[O-]c1ccc([N+](=O)[O-])cc1</chem>

The para nitro group withdraws electron density through both induction and resonance, stabilizing the conjugate base and increasing acidity. The methyl group donates electron density, making the corresponding phenol less acidic than unsubstituted phenol.

Therefore,

$$\text{acidity: } F > D > E.$$

Following the stated relationship between acidity and gel binding,

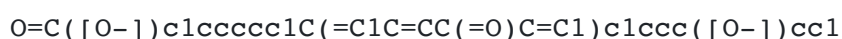
$$\boxed{\text{binding affinity: } F > D > E}.$$

The phenolic hydrogen can form a hydrogen bond to an amide carbonyl oxygen in the gel; the more acidic phenols are stronger donors in this interaction.

1.7

Neutral **phenolphthalein**, O=C1OC(c2ccc(O)cc2)(c2ccc(O)cc2)c2ccccc21, contains a closed lactone ring and a tetrahedral central carbon. That carbon interrupts conjugation between the phenol-derived rings.

In the stated basic indicator range, removal of two protons and opening of the lactone ring give the **quinonoid phenolphthalein dianion H**:



The balanced net ionic equation is



Here hydroxide, [OH-], is supplied by aqueous sodium hydroxide, [Na+] . [OH-].

To draw the displayed resonance contributor precisely:

- Open the lactone by breaking the bond between its ring oxygen and the central carbon. The resulting carboxylate group is ortho to the central-carbon substituent on the original fused benzene ring.
- Connect the central carbon by single bonds to that benzene ring and to a para-phenoxide ring.
- Double-bond the central carbon to the second phenol-derived ring. Draw this ring in quinonoid form, with a carbonyl group para to the exocyclic double bond and two internal C=C bonds.
- Place one negative charge on the phenoxide oxygen and one on a carboxylate oxygen, giving an overall charge of 2[−].

Electron donation from a deprotonated phenolic oxygen, accompanied by shifts of the ring π bonds and cleavage of the lactone bond, produces this conjugated arrangement. An equivalent resonance contributor exchanges the carbonyl and phenoxide roles of the two phenol-derived rings.

The SMILES represents one contributor; the actual electronic structure has delocalized bonding and charge. The central carbon is now trigonal planar, allowing extended conjugation that shifts absorption into the visible region and produces the reddish pink colour.

1.8

The correct reagent is **phthalic anhydride**, O=C1OC(=O)c2ccccc21, corresponding to **(e)**.

Its cyclic anhydride supplies the two adjacent carbonyl-derived carbon atoms required for the lactone framework. Acid activation permits condensation with phenol, whose hydroxyl group directs substitution to the para position. Incorporation of two phenol molecules and lactone formation give phenolphthalein.

The balanced overall reaction is



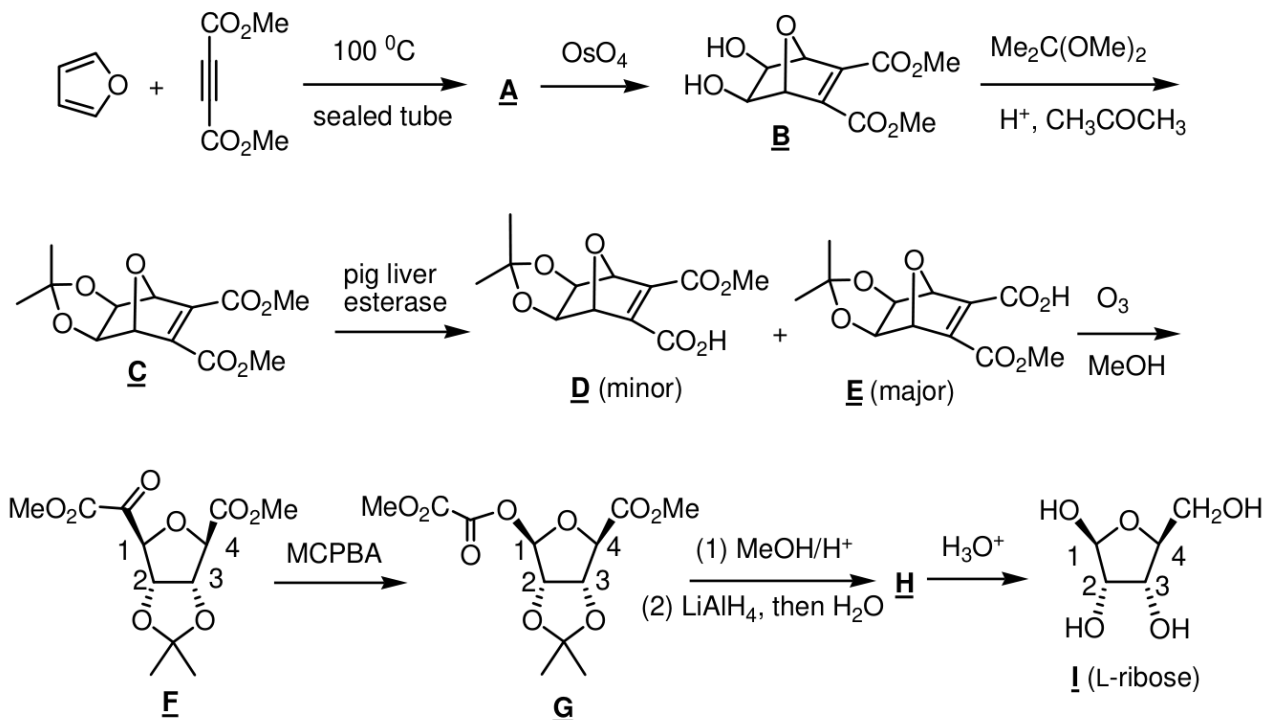
The reactants and product are phthalic anhydride, phenol Oc1ccccc1, and phenolphthalein O=C1OC(c2ccc(O)cc2)(c2ccc(O)cc2)c2ccccc21, respectively.

The stated conditions are concentrated sulfuric acid, OS(=O)(=O)O, at 180 °C for 5 h. The acid promotes the condensation and is not consumed in the net equation. Starting from the anhydride gives **one water molecule** as the net byproduct.

The solution was checked against the official solution.

Problem 2: Organic Synthesis and Stereochemistry

Natural carbohydrates are generally produced by photosynthesis in plants. However, unnatural carbohydrates can be prepared by organic synthesis. The following outline is a synthetic scheme for the unnatural L-ribose (compound **I**).



2.1 Compound **A** has the molecular formula of $C_{10}H_{10}O_5$. Draw the structural formula of **A**.

2.2 Given the chemistry described for reaction sequence **A** to **C**, indicate whether the following statements are true or false (Use T to represent true and F to represent false).

- ___ (a) OsO_4 is an oxidizing agent in the reaction of **A** to **B**.
- ___ (b) MeOH is generated as a by-product in the reaction of **B** to **C**.
- ___ (c) Protons act as the catalyst in the transformation of **B** to **C**.
- ___ (d) **C** will still be formed albeit in lower yields in the absence of $Me_2C(OMe)_2$.

Pig liver esterase is an enzyme that can hydrolyze esters to carboxylic acids. Hydrolysis of **C** by the pig liver esterase afforded an enantiomeric mixture of **D** and **E**, in which **E** was the major component. The optical rotation of the mixture was $[\alpha]_D^{20} = -37.1^\circ$. Further purification by recrystallization gave pure **E** with the optical rotation $[\alpha]_D^{20} = -49.0^\circ$.

2.3 What is the molar ratio of **D/E** in the product mixture before the recrystallization? Show your work.

2.4 Reaction of **F** with meta-chloroperoxybenzoic acid (MCPBA) afforded **G** as the product. Indicate whether the following statements are true or false (Use T to represent true and F to represent false).

- ___ (a) The reaction was to oxidize compound **F**.
- ___ (b) The oxygen atom inserted originated from MCPBA.
- ___ (c) The *R/S* notation of C-1 remained unchanged before and after the reaction.

The molecular formula of **H** is $C_9H_{16}O_5$. Proton NMR data of **H** are listed as follows:

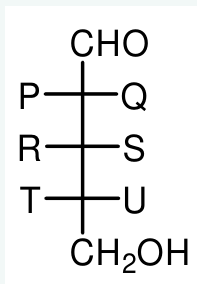
^1H NMR ($CDCl_3$) δ 1.24 (s, 3H), 1.40 (s, 3H), 3.24 (m, 1H), 3.35 (s, 3H), 3.58 (m, 2H), 4.33 (m, 1H); 4.50 (d, $J = 6$ Hz, 1H), 4.74 (d, $J = 6$ Hz, 1H), 4.89 (s, 1H).

2.5 Draw the configurational formula of **H**.

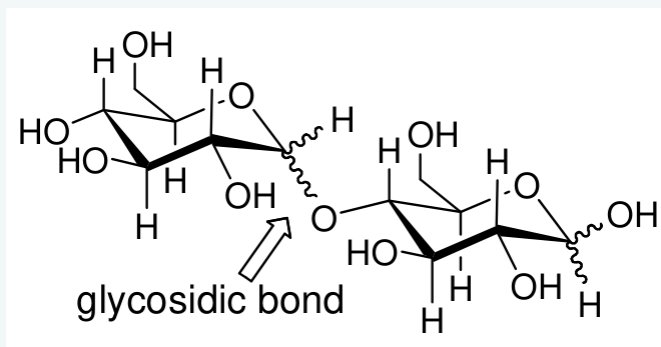
2.6 Assign R/S notations for compound **I** at C-1, C-2, C-3 and C-4. Give your answers as follows:

C-1: ; **C-2**: ; C-3: ; **C-4**: .

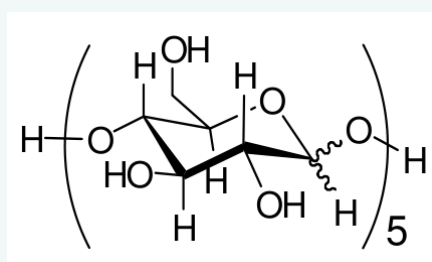
2.7 What are the identities of P, Q, R, S, T and U in the Fischer projection of compound **I** (L-ribose)?



Disaccharides are compounds with two monosaccharide subunits linked together by a glycosidic bond. Polysaccharides contain as few as ten, or as many as thousands, monosaccharide subunits. An example of a disaccharides is as follows:



2.8 How many diastereoisomers would be obtained for pentasaccharide **J**, if it is derived from five units of D-glucose?



pentasaccharide **J** derived from D-glucose

Official English text of the problem.

Answers

- 2.1 **A** is **dimethyl 7-oxabicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate**:
COC(=O)C1=C(C(=O)OC)[C@H]2C=C[C@@H]1O2
- 2.2 (a) **T**; (b) **T**; (c) **T**; (d) **T**.

- **2.3** $D/E = 0.138$, or $D : E = 1 : 7.24$. The mixture contains approximately **12.1 mol% D** and **87.9 mol% E**.
- **2.4** (a) **T**; (b) **T**; (c) **F**. C-1 changes from *S* in **F** to *R* in **G**, despite retention of its spatial configuration.
- **2.5 H** is **methyl 2,3-O-isopropylidene-β-L-ribofuranoside**:
CO[C@H]1O[C@@H](CO)[C@@H]2OC(C)(C)O[C@H]12
 In the orientation used for **G**, draw the C-1 methoxy group and C-4 hydroxymethyl group on solid wedges; retain the dashed bonds from C-2 and C-3 to the acetonide oxygens.
- **2.6** $C-1: S; \quad C-2: S; \quad C-3: R; \quad C-4: S$.
 The illustrated **I** is **β-L-ribofuranose**:
O[C@H]1O[C@@H](CO)[C@H](O)[C@@H]1O
- **2.7** $P = R = T = OH; \quad Q = S = U = H$. All three hydroxyl groups are on the left of the Fischer projection.
- **2.8** $2^5 = 32$ diastereoisomeric configurations.

Solution

2.1 — Identification of A

Furan, c1ccoc1, reacts with dimethyl acetylenedicarboxylate, COC(=O)C#CC(=O)OC, by a **Diels–Alder cycloaddition**. Furan supplies the four-electron diene, and the alkyne supplies the two-electron dienophile.

The atom-balanced reaction is



No atoms are eliminated. One π bond remains between the two former alkyne carbons, and another remains between the two internal carbons of the furan diene. The original furan oxygen becomes the bridge of the bicyclic product.

To draw **A**, take the structure of **B**, remove its two hydroxyl groups, and restore a double bond between the carbons that carried them. The two methyl ester groups remain attached to the other double bond. This gives the bicyclic structure named and encoded in Answer 2.1.

2.2 — Oxidation and diol protection

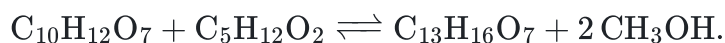
(a) True. Osmium tetroxide, O=[Os](=O)(=O)=O, effects **syn dihydroxylation** of the unsubstituted double bond of **A**, producing the cis vicinal diol **B**. The organic substrate undergoes a two-electron oxidation.

A balanced oxidation half-equation is



(b) True. The two hydroxyl groups of **B** react with **2,2-dimethoxypropane**, COC(C)(C)OC, to form the cyclic isopropylidene ketal, or **acetonide**, of **C**. Both methoxy groups of the reagent can leave as **methanol**, CO.

The balanced net equation is



Thus two molecules of methanol are formed per acetone formed by this net reaction.

(c) True. Protonation facilitates cleavage of a methoxy group and subsequent substitution by the diol oxygens. Deprotonation regenerates the acid catalyst. Protons are therefore catalytic, rather than consumed stoichiometrically.

(d) True. Acetone, $\text{CC}(=\text{O})\text{C}$, is also present and can itself react with the diol under acid catalysis:



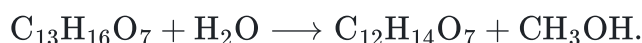
This equilibrium produces water, O , which promotes the reverse reaction. The dimethoxy reagent helps drive acetone formation; it can also consume water according to



Consequently, acetone and acid can still produce **C** without 2,2-dimethoxypropane, but less efficiently under the stated conditions.

2.3 — Enantiomeric composition

The esterase hydrolyzes one methyl ester group:



Because **D** and **E** are enantiomers, their specific rotations under identical conditions have equal magnitudes and opposite signs:

$$[\alpha]_D = +49.0^\circ, \quad [\alpha]_E = -49.0^\circ.$$

Let their mole fractions be x_D and x_E . Their molar masses are identical, so the specific rotation is weighted by these same fractions:

$$\begin{aligned} x_D + x_E &= 1, \\ -37.1^\circ &= x_D(49.0^\circ) + x_E(-49.0^\circ). \end{aligned}$$

Therefore,

$$x_E - x_D = \frac{37.1}{49.0} = 0.75714.$$

The enantiomeric excess in favour of **E** is consequently 75.7%, and

$$x_D = \frac{1 - 0.75714}{2} = 0.12143, \quad x_E = \frac{1 + 0.75714}{2} = 0.87857.$$

Hence

$$\frac{n_D}{n_E} = \frac{49.0 - 37.1}{49.0 + 37.1} = \frac{11.9}{86.1} = 0.138$$

or

$$D : E = 1 : 7.24.$$

2.4 — Baeyer–Villiger oxidation and C-1 configuration

The relevant structures are:

Compound	Structural description	Stereochemical SMILES
F	Protected ribofuranosyl α -keto ester	<chem>COC(=O)C(=O)[C@H]1O[C@@H](C(=O)OC)[C@@H]2OC(C)(C)O[C@H]12</chem>
G	Corresponding protected ribofuranosyl methyl oxalate	<chem>COC(=O)C(=O)O[C@H]1O[C@@H](C(=O)OC)[C@@H]2OC(C)(C)O[C@H]12</chem>

The reagent is **3-chloroperoxybenzoic acid**, O=C(OO)c1cccc(Cl)c1. Its reduction product is **3-chlorobenzoic acid**, O=C(O)c1cccc(Cl)c1.

Writing *R* for the protected sugar residue attached through C-1, the balanced transformation is
 $R-C(=O)-C(=O)-OMe + m\text{-ClC}_6\text{H}_4\text{CO}_3\text{H} \longrightarrow R-O-C(=O)-C(=O)-OMe + m\text{-ClC}_6\text{H}_4\text{CO}_2\text{H}.$

(a) True. This is a **Baeyer–Villiger oxidation**: oxygen is inserted between C-1 of the sugar and the adjacent ketone carbonyl carbon.

(b) True. The inserted oxygen comes from the terminal peroxide oxygen of MCPBA. Mechanistically, peracid addition gives a Criegee intermediate; migration of the sugar group accompanies cleavage of the peroxide bond.

(c) False. Migration occurs with **retention of spatial configuration** at the migrating C-1, but its CIP priorities change.

Compound	C-1 priorities, highest to lowest	Configuration
F	Ring oxygen > acyl carbon > C-2 > H	<i>S</i>
G	Exocyclic oxalate oxygen > ring oxygen > C-2 > H	<i>R</i>

In **F**, the acyl carbon outranks C-2 because its next attached-atom list is (O, O, C), compared with (O, C, H) for C-2.

In **G**, both leading substituents begin with oxygen. The exocyclic oxygen leads to a carbonyl carbon and outranks the ring oxygen, which leads to saturated C-4.

Thus the two highest priorities exchange their spatial positions:



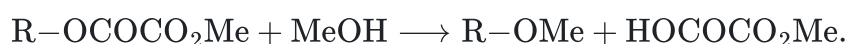
without inversion of the stereocenter.

2.5 — Identification and configuration of H

The two operations convert the substituents of **G** as follows:

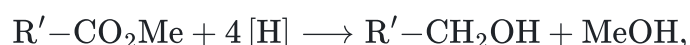
1. Acidic methanol converts the anomeric oxalate ester into a **methyl glycoside**.
2. **Lithium aluminium hydride**, $[Li^+].[AlH_4^-]$, reduces the methyl ester attached to C-4 to a hydroxymethyl group. The acetonide remains intact.

A balanced net representation of the first functional-group change is



Here the oxalate-derived coproduct is **methyl hydrogen oxalate**, COC(=O)C(=O)O.

The ester reduction can be represented by



where $[H]$ denotes a formal reducing hydrogen equivalent.

These transformations give **methyl 2,3-O-isopropylidene- β -L-ribofuranoside**, the structure in Answer 2.5. Its formula follows directly from its groups:

- Five carbons in the sugar skeleton.
- Three carbons in the acetonide.
- One carbon in the methoxy group.
- Five oxygens: one ring oxygen, two acetonide oxygens, one methoxy oxygen, and one alcohol oxygen.

Thus its molecular formula is $C_9H_{16}O_5$, as required.

The proton NMR data support this assignment:

δ / ppm	Integral and multiplicity	Assignment
1.24, 1.40	Two singlets, 3H each	The two nonequivalent acetonide methyl groups
3.24	Multiplet, 1H	Alcohol OH proton
3.35	Singlet, 3H	Anomeric methoxy group
3.58	Multiplet, 2H	CH_2OH
4.33	Multiplet, 1H	H-4
4.50, 4.74	Two doublets, $J = 6$ Hz, 1H each	Mutually coupled H-2 and H-3
4.89	Singlet, 1H	Anomeric H-1

The integrations total 16 hydrogens. The anomeric singlet is consistent with the very small H-1/H-2 coupling of the β anomer in this acetonide-constrained furanose. The absolute stereochemistry is supplied by the synthetic sequence.

For the requested drawing, retain the five-membered sugar ring and the 2,3-acetonide of **G**. Replace the C-1 oxalate substituent by a **solid-wedge methoxy group**, and replace the C-4 methyl ester by a **solid-wedge hydroxymethyl group**. The two bonds from C-2 and C-3 to the acetonide oxygens remain dashed.

The subsequent acid hydrolysis removes both protecting groups:



2.6 — Absolute configurations of I

Apply the CIP rules to the **cyclic structure actually drawn**.

Center	Priorities, highest to lowest	Result
C-1	Ring oxygen > hydroxyl oxygen > C-2 > H	<i>S</i>
C-2	Hydroxyl oxygen > C-1 > C-3 > H	<i>S</i>
C-3	Hydroxyl oxygen > C-4 > C-2 > H	<i>R</i>
C-4	Ring oxygen > C-3 > hydroxymethyl carbon > H	<i>S</i>

The distinction at **C-3** deserves attention. Both adjacent carbons initially present the list (O, C, H). Following their oxygen branches breaks the tie:

- The oxygen reached through C-4 is bonded onward to carbon.

- The hydroxyl oxygen reached through C-2 is bonded to hydrogen.

Therefore C-4 outranks C-2.

The answer for the illustrated β -L-ribofuranose is

$$\boxed{(1S, 2S, 3R, 4S)}.$$

Free L-ribose can equilibrate between forms in solution; these assignments refer specifically to **I as drawn**.

2.7 — Fischer projection of L-ribose

Open-chain **L-ribose**, systematically **(2S,3S,4S)-2,3,4,5-tetrahydroxypentanal**, has SMILES

O=C[C@H](O)[C@H](O)[C@H](O)CO.

With the aldehyde group at the top and the hydroxymethyl group at the bottom, **all three hydroxyl groups lie on the left**, and all three hydrogens lie on the right. Consequently,

$$\boxed{P = R = T = \text{OH}}, \quad \boxed{Q = S = U = \text{H}}.$$

Here a hydroxyl substituent can be represented as $[*]O$, with $*$ denoting its attachment to the carbon skeleton; hydrogen is $[H]$.

The open-chain C-3 descriptor is *S*, whereas cyclic **I** has C-3 *R*. Ring closure changes the CIP ordering of the two carbon paths; it does not require inversion at that carbon.

2.8 — Number of pentasaccharide diastereoisomers

The D-glucose units fix the configurations of their nonanomeric stereocenters. Each of the five anomeric carbons can independently have either configuration:

- Four occur at glycosidic linkages.
- The fifth is the free anomeric center at the reducing end.

The linkage pattern is fixed by the drawing. The chain ends are different, so reversing the sequence does not identify otherwise distinct configurations.

Therefore,

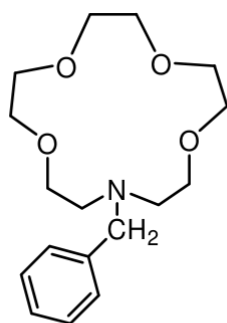
$$N = 2^4 \times 2 = \boxed{32}.$$

They are diastereoisomers because changing these anomeric configurations leaves the other D-glucose stereocenters unchanged.

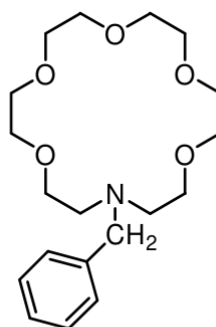
The solution was checked against the official solution.

Problem 3: Organic Photochemistry and Photophysics

Crown ethers show size-dependent binding capability to alkali metal ions. For example, the azacrowns **A** and **B** exhibit different binding constants for Na^+ , K^+ , and Cs^+ .



A

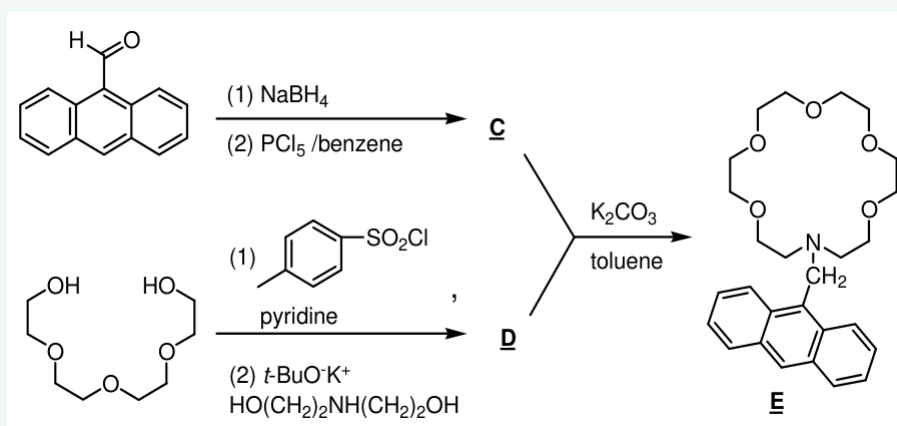


B

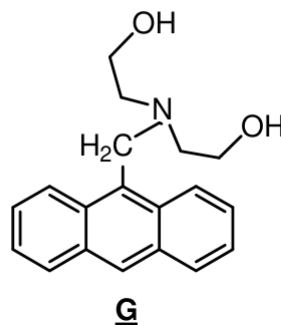
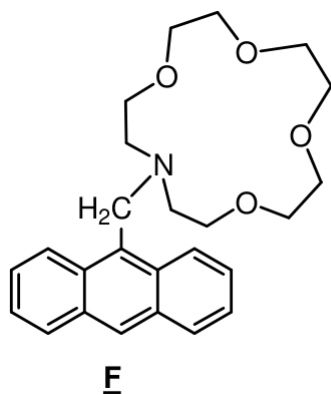
Metal ion	Radius (pm)	Binding constant ($\log_{10} K$)	
		Compound A	Compound B
Na^+	98	2.49	3.57
K^+	133	1.83	5.00
Cs^+	165	1.37	3.39

Anthracene exhibits strong fluorescence with emission wavelength centered at 325 nm. Combining the binding selectivity of azacrowns for alkali metal ions and the highly fluorescent anthracene, a metal ion selective fluorescent sensor **E** has been developed.

3.1 Provide the structural formula of **C** and **D** in the following synthesis.



For comparison studies, the anthracene derivatives **F** and **G** shown below were also synthesized. These compounds **E**, **F**, and **G** are almost non-fluorescent in neutral conditions due to the strong photoinduced electron transfer (PET) quenching process arising by donating nitrogen lone-pair electron to the anthracene excited-state.



3.2 Upon adding aqueous HCl , which compound will exhibit strong fluorescence? Select your answer from the following choices.

- (a) none of them (b) **E** and **F** only (c) **G** only (d) all of them

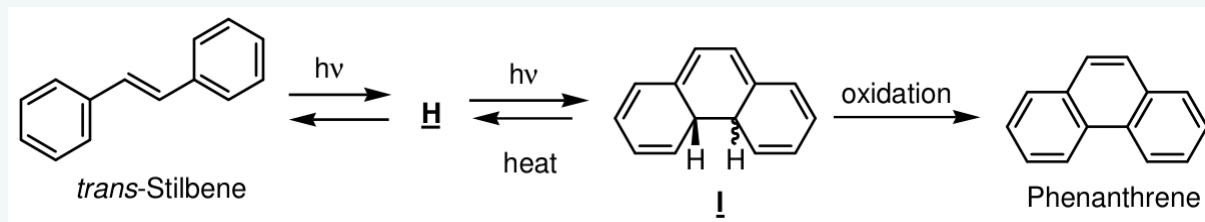
3.3 By adding one equivalent of potassium acetate into a dilute solution ($1 \times 10^{-5} \text{ M}$) of **E**, **F**, and **G** in methanol, respectively, which compound will show the strongest fluorescence? Select your answer from the following choices.

- (a) **E** (b) **F** (c) **G**

3.4 Upon adding one equivalent of metal acetate to a dilute solution of **F**, which metal acetate will cause the strongest fluorescence? Select your answer from the following choices.

- (a) sodium acetate (b) potassium acetate (c) cesium acetate (d) doesn't make any difference

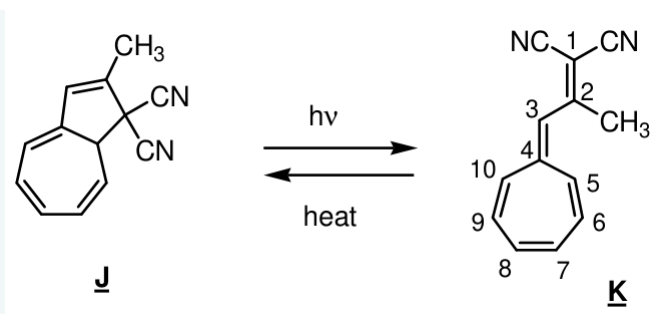
Upon irradiation with ultraviolet light, *trans*-stilbene is transformed into an intermediate **H**, which undergoes a photocyclization to form dihydrophenanthrene **I**. Further oxidation of **I** gives phenanthrene.



3.5 Draw the structural formula of compound **H**?

3.6 What is the relative stereochemistry of the two H-atoms shown (cis or trans) in compound **I**?

Dihydroazulene derivative **J** exhibits interesting photochromic behavior. Upon irradiation, colorless dihydroazulene **J** undergoes photoinduced rearrangement to the corresponding vinylheptafulvene **K**. The vinylheptafulvene undergoes thermal reversion to dihydroazulene.



3.7 Which compound will absorb light with longer wavelength? Select your answer from the following choices: (a) **J** (b) **K**

3.8 Compound **K** can react with one equivalent of $\text{CF}_3\text{CO}_2\text{H}$ to generate a stable aromatic salt. Which position of **K** is most likely protonated? Select your answer from the following choices.

(a) C-2 (b) C-3 (c) C-4 (d) C-5

Official English text of the problem.

Answers

- **3.1:** **C** is **9-(chloromethyl)anthracene**; **D** is **1-aza-18-crown-6**.
- **3.2:** (d) All of them: **E**, **F**, and **G**.
- **3.3:** (a) **E**.
- **3.4:** (a) Sodium acetate.
- **3.5:** **H** is **cis-stilbene**, or **(Z)-1,2-diphenylethene**.
- **3.6:** trans.
- **3.7:** (b) **K**.
- **3.8:** (b) **C-3**, giving a substituted tropylium salt.

Solution

3.1 — Identification of **C** and **D**

C is **9-(chloromethyl)anthracene**, SMILES C1Cc1c2ccccc2cc2ccccc12.

The starting aldehyde is **anthracene-9-carbaldehyde**, O=Cc1c2ccccc2cc2ccccc12. Sodium borohydride reduces its aldehyde group to a primary alcohol, giving **(anthracen-9-yl)methanol**, OCc1c2ccccc2cc2ccccc12. Phosphorus pentachloride then replaces the hydroxyl group with chlorine.

Let **R** denote the anthracen-9-yl group. Including hydrolysis during work-up, a balanced net reduction is



The chlorination is



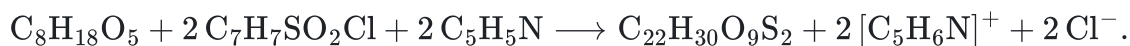
Thus, the drawing of **C** should show three linearly fused aromatic rings, with a $-\text{CH}_2\text{Cl}$ substituent at carbon 9 of anthracene.

D is **1-aza-18-crown-6**, SMILES [NH]1CCOCCOCCOCCOCCOCC1.

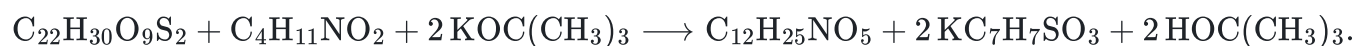
The starting polyether is **tetraethylene glycol**, OCCOCCOCCOCCO. Its two terminal hydroxyl groups are converted into tosylates by **p-toluenesulfonyl chloride**, Cc1ccc(S(=O)(=O)C1)cc1, in pyridine.

The resulting **tetraethylene glycol ditosylate** has SMILES Cc1ccc(S(=O)(=O)OCCOCCOCCOCCOS(=O)(=O)c2ccc(C)cc2)cc1.

With pyridine trapping the hydrogen chloride, the balanced reaction is



Potassium tert-butoxide generates alkoxide groups from the two hydroxyl groups of **diethanolamine**, OCCNCCO. These displace the two terminal tosylate groups, forming two new carbon–oxygen bonds and closing the macrocycle:



The product C_{12}H_{25}NO_5 is **D**. Draw an **18-membered ring containing five oxygen atoms and one NH group**, with every successive pair of heteroatoms separated by two methylene groups. The nitrogen retains its hydrogen during this cyclization.

Finally, the secondary amine **D** attacks the chloromethyl carbon of **C**. Carbonate removes the nitrogen proton, producing the tertiary amine **E**, **N-(anthracen-9-ylmethyl)-1-aza-18-crown-6**:

SMILES N1(Cc2c3cccc3cc3cccc23)CCOCCOCCOCCOCCOCC1

A balanced overall equation, including carbonate neutralization, is



Here the organic reactants are **C** and **D**, and the organic product is **E**.

3.2 — Fluorescence after adding hydrochloric acid

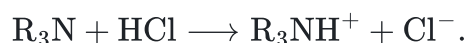
The answer is **(d)**, all three compounds.

Besides **E**, the compounds are:

- **F: N-(anthracen-9-ylmethyl)-1-aza-15-crown-5**,
SMILES N1(Cc2c3cccc3cc3cccc23)CCOCCOCCOCCOCC1
- **G: N-(anthracen-9-ylmethyl)diethanolamine**,
SMILES OCCN(Cc1c2cccc2cc2cccc12)CCO

In each neutral compound, the tertiary-amine nitrogen has a lone pair that can donate an electron to excited anthracene. This PET process competes with fluorescence and quenches it.

Hydrochloric acid protonates the nitrogen:



The nitrogen-protonated products are:

Ion	Name	SMILES
EH^+	N-protonated E	<chem>[NH+]1(Cc2c3cccc3cc3cccc23)CCOCCOCCOCCOCCOCC1</chem>
FH^+	N-protonated F	<chem>[NH+]1(Cc2c3cccc3cc3cccc23)CCOCCOCCOCCOCC1</chem>
GH^+	N-protonated G	<chem>OCC[NH+](Cc1c2cccc2cc2cccc12)CCO</chem>

Protonation uses the nitrogen lone pair to form the new nitrogen–hydrogen bond. Nitrogen can therefore no longer act as the same electron donor, PET is suppressed, and strong anthracene fluorescence is restored in **E**, **F**, and **G**.

3.3 — Fluorescence after adding potassium acetate

The answer is **(a)**, **E**.

The reference hosts are:

- **A: N-benzyl-1-aza-15-crown-5**, N1(Cc2ccccc2)CCOCCOCCOCCOCC1
- **B: N-benzyl-1-aza-18-crown-6**, N1(Cc2ccccc2)CCOCCOCCOCCOCCOCC1

E contains the same aza-18-crown-6 binding unit as **B**, whereas **F** contains the smaller aza-15-crown-5 unit of **A**. For potassium binding to these reference hosts,

$$\log_{10} K_B = 5.00, \quad \log_{10} K_A = 1.83,$$

so

$$\frac{K_B}{K_A} = 10^{5.00-1.83} \approx 1.5 \times 10^3.$$

Thus, the larger crown provides a much more favourable binding site for **potassium(I)**, [K⁺]. **G** lacks the preorganized macrocyclic cavity.

Potassium binding engages the crown's nitrogen and oxygen donors and reduces the nitrogen lone pair's ability to participate in PET. Consequently, **E** shows the strongest fluorescence enhancement. The coordination contacts and folded crown conformation are described here in words; they are not encoded by the neutral ligand's SMILES.

The numerical ratio above applies to **A** and **B** as tabulated. It supports the receptor comparison without assuming exact binding constants for **E** and **F**.

3.4 — Metal-ion selectivity of F

The answer is **(a)**, **sodium acetate**, SMILES CC(=O)[O-].[Na+].

F has the smaller aza-15-crown-5 receptor of **A**. The given binding constants for **A** follow

$$\log_{10} K(\text{Na}^+) = 2.49 > \log_{10} K(\text{K}^+) = 1.83 > \log_{10} K(\text{Cs}^+) = 1.37.$$

The smaller sodium ion, with radius 98 pm, fits this receptor most favourably. Sodium binding therefore produces the greatest suppression of PET, and hence the strongest fluorescence, among the three salts.

3.5 — Structure of H

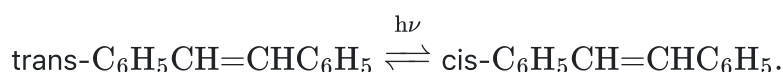
H is **cis-stilbene**, also called **(Z)-1,2-diphenylethene**:

c1ccccc1/C=C\c1ccccc1

The starting **trans-stilbene**, or **(E)-1,2-diphenylethene**, has SMILES

c1ccccc1/C=C/c1ccccc1.

Light permits isomerization about the central alkene:



Draw **H** with the two phenyl groups on the **same side** of the carbon–carbon double bond. This configuration allows the two ortho positions that will form the new bond to approach one another in the reactive conformation.

3.6 — Relative stereochemistry in I

The two indicated hydrogens are **trans**.

The ring closure uses a conjugated **six- π -electron system**. A photochemical 6π electrocyclization is **conrotatory**: the two terminal orbital systems rotate in the same sense. Applied to the reactive conformation of cis-stilbene, this places the two ring-junction hydrogens on opposite faces.

The product is **trans-4a,4b-dihydrophenanthrene**. A stereochemical SMILES for one enantiomer is C1=CC=C[C@H]2C1=CC=C1C=CC=C[C@@H]12.

Opposite conrotation gives its mirror image. In the requested drawing, show **one indicated hydrogen on a solid wedge and the other on a hashed wedge**.

The photocyclization conserves the molecular formula $C_{14}H_{12}$. Subsequent oxidation removes the two ring-junction hydrogens and gives **phenanthrene**, c1ccc2c(c1)ccc1ccccc12. Because no oxidant is specified, its balanced oxidation half-reaction is



3.7 — Longer-wavelength absorption

The answer is **(b), K**.

The structures are:

- **J: 1,1-dicyano-2-methyl-1,8a-dihydroazulene**,
CC1=CC2=CC=CC=CC2C1(C#N)C#N
- **K: the vinylheptafulvene**, systematically **2-[1-(cyclohepta-2,4,6-trien-1-ylidene)propan-2-ylidene]propanedinitrile**,
N#CC(C#N)=C(C)C=C1C=CC=CC=C1

The absolute configuration of **J** is not specified in the drawing and is therefore left unspecified in its SMILES.

In **J**, the tetrahedral dicyano-substituted carbon and the saturated ring-junction carbon interrupt conjugation. Ring opening gives **K**, with a more extensive conjugated system that includes the dicyano-substituted end of the molecule.

This lowers the relevant electronic excitation energy. Since

$$\Delta E = \frac{hc}{\lambda},$$

the smaller excitation energy corresponds to a longer absorption wavelength:

$$\lambda_{\max,K} > \lambda_{\max,J}.$$

3.8 — Protonation of K

The answer is **(b), C-3**.

The relevant connectivity in **K** is



where the chain CH is **C-3** and the attached ring carbon is **C-4**.

The electrons of the $\text{C}_3=\text{C}_4$ bond form a bond between **C-3** and the proton. Consequently:

- C-3 becomes CH_2 .
- The C-3–C-4 bond becomes a single bond.
- A positive charge is initially placed at C-4.

The seven-membered ring now has three double bonds and an empty p orbital at C-4. All seven ring atoms participate in a continuous cyclic conjugated system containing **six π electrons**:

$$6 = 4n + 2, \quad n = 1.$$

The product is therefore an aromatic **substituted tropylium ion**.

With **trifluoroacetic acid**, $\text{O}=\text{C}(\text{O})\text{C}(\text{F})(\text{F})\text{F}$, the balanced reaction is



The resulting **C-3-protonated K trifluoroacetate**, a substituted tropylium salt, has SMILES

N#CC(C#N)=C(C)C[C+]1C=CC=CC=C1.O=C([O-])C(F)(F)F.

This SMILES depicts one localized resonance contributor. In the actual aromatic cation, the positive charge is delocalized around the seven-membered ring. The drawing should show the side chain attached through a single bond to that ring, with C-3 now bearing two hydrogens.

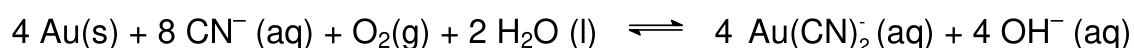
The solution was checked against the official solution.

Problem 4: Gold Capital of Asia

A

Gold Capital of Asia

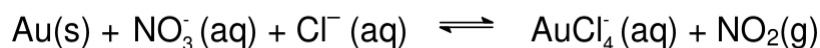
Chiufen, the old mining town located within the hills in the northeast Taiwan, is a place where you can really experience Taiwan's historical legacy. It was the site of one of the largest gold mines in Asia. Accordingly, Chiufen is often referred to as the Gold Capital of Asia. The compound KCN is traditionally used to extract gold from ore. Gold dissolves in cyanide (CN^-) solutions in the presence of air to form $\text{Au}(\text{CN})_2^-$, which is stable in aqueous solution.



4.A-1 Draw a structure for $\text{Au}(\text{CN})_2^-$ showing the spatial arrangements of the atoms.

4.A-2 How many grams of KCN are needed to extract 20 g of gold from ore? Show your work.

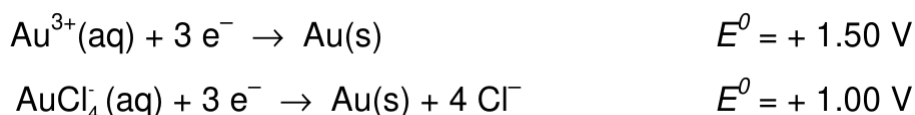
Aqua regia, a 3 : 1 mixture (by volume) of concentrated hydrochloric acid and nitric acid, was developed by the alchemists as a means to "dissolve" gold. The process is actually a redox reaction with the following simplified chemical equation:



4.A-3 Write down the half reactions, and use them to obtain a balanced redox reaction for this process.

4.A-4 What are the oxidizing and reducing agents for 4.A-3 process?

Gold is too noble to react with nitric acid. However, gold does react with aqua regia because the complex ion AuCl_4^- forms. Consider the following half-reactions:



An electrochemical cell can be formed from these two redox couples.

4.A-5 Calculate the formation constant for AuCl_4^- at 25 °C:

$$K = \frac{[\text{AuCl}_4^-]}{[\text{Au}^{3+}][\text{Cl}^-]^4}$$

4.A-6 The function of HCl is to provide Cl^- . What is the purpose of the Cl^- for the above reaction. Select your answer from the following choices.

- (a) Cl^- is an oxidizing agent
- (b) Cl^- is a reducing agent
- (c) Cl^- is a complexing agent
- (d) Cl^- is a catalyst

B

Gold Nanoparticles

The synthesis and characterization of gold nanoparticles is currently an active research area. The Brust-Schiffrin method for the synthesis of gold nanoparticle (AuNP) allows the facile preparation of thermally stable and air-stable AuNPs of reduced polydispersity with a controlled size distribution ranging in diameter between 1.5 and 5.2 nm. The preparative procedure is briefly described as follows. An aqueous solution of HAuCl_4 is mixed with a toluene solution of tetra-n-octylammonium bromide. The solution is mixed with dodecanethiol and is treated with an excess of NaBH_4 . Formation of the AuNPs is evidenced by the immediate, pronounced darkening of the toluene phase. After ca. 24 h, the toluene solvent is removed with a rotary evaporator and the resulting solid washed on a frit with ethanol and hexane to remove excess thiol. These AuNPs can be repeatedly isolated and re-dissolved in common organic solvents without irreversible aggregation or decomposition.

4.B-1 Is the methodology for this fabrication referred to a top-down or a bottom-up approach? Select your answer from the following choices.

- (a) top-down approach, which entails reducing the size of the smallest structures to the nanoscale
- (b) bottom-up approach, which involves manipulating individual atoms and molecules into

nanostructures

4.B-2 The trimethyl-n-octylammonium bromide can also be used as a phase-transfer reagent. It can carry AlCl_4^- from an aqueous phase to an organic phase. Which property does trimethyl-n-octylammonium bromide possess to function as an efficient phase-transfer reagent? Select your answer from the following choices.

- (a) one side of the molecule is electropositive, the other side is electronegative.
- (b) one side of the molecule is hydrophilic, the other side is hydrophobic.
- (c) one side of the molecule is acidic, the other side is basic.

4.B-3 What is the function of NaBH_4 in this preparation? Select your answer from the following choices.

- (a) reducing agent
- (b) oxidizing agent
- (c) neutralization agent
- (d) complexing agent

4.B-4 If the average diameter of a gold nanoparticle is 3 nm, what is the estimated number of Au atoms in each nanoparticle? (the atomic radius of Au is 0.144 nm). Select your answer from the following choices and show your work.

- (a) 10^2
- (b) 10^3
- (c) 10^4
- (d) 10^5

4.B-5 What is the estimated percentage of Au atoms on the surface of a nanoparticle? Select your answer from the following choices and show your work.

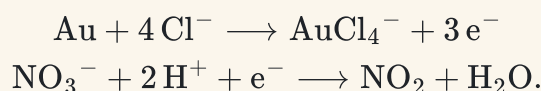
- (a) 20 – 30 %
- (b) 40 – 50 %
- (c) 60 – 70 %
- (d) 80 – 90 %

Official English text of the problem.

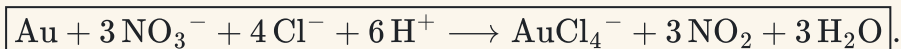
Answers

- **4.A-1:** Dicyanidoaurate(I), $\text{Au}(\text{CN})_2^-$, SMILES $\text{N}\# \text{C}[\text{Au-}]\text{C}\# \text{N}$. All five atoms lie on a straight line in the order nitrogen–carbon–gold–carbon–nitrogen; the carbon–gold–carbon angle is 180° .
- **4.A-2:** 13.2 g of potassium cyanide, KCN , $[\text{K}^+].[\text{C-}]\# \text{N}$; approximately 13 g to two significant figures.

- **4.A-3:** The half-reactions are



Their balanced sum is



- **4.A-4:** Oxidizing agent: nitrate ion, NO_3^- , $[\text{O}-][\text{N}+](=\text{O})[\text{O}-]$. Reducing agent: elemental gold, $\text{Au}(\text{s})$; $[\text{Au}]$ represents an individual gold atom.
- **4.A-5:** $K \approx 2.3 \times 10^{25}$ for formation of tetrachloridoaurate(III), AuCl_4^- , $[\text{Au}-](\text{Cl})(\text{Cl})(\text{Cl})\text{Cl}$.
- **4.A-6: (c)** — chloride ion, Cl^- , $[\text{Cl}-]$, is a complexing agent.
- **4.B-1: (b)** — bottom-up approach.
- **4.B-2: (b)** — a hydrophilic charged head and a hydrophobic hydrocarbon tail.
- **4.B-3: (a)** — sodium borohydride, NaBH_4 , $[\text{Na}+].[\text{BH}_4-]$, is a reducing agent.
- **4.B-4: (b)** — approximately 10^3 gold atoms per nanoparticle.
- **4.B-5: (b)** — 40–50%; the outer-layer estimate gives approximately 47%.

Solution

The SMILES below specify connectivity and formal charge. Formal charges assigned to metals in these covalent SMILES representations are not their oxidation states; coordination geometries are stated separately.

4.A-1

Each cyanide ion, CN^- , $[\text{C}-]\# \text{N}$, has charge -1 . Therefore the oxidation state x of gold satisfies

$$x + 2(-1) = -1, \quad x = +1.$$

The two-coordinate gold(I) center has a d^{10} electron configuration and linear coordination. Both cyanide ligands bind through their carbon atoms.

The drawing should therefore show the **dicyanidoaurate(I) ion**, $\text{N}\# \text{C}[\text{Au}-]\text{C}\# \text{N}$, as



Draw all five atoms on one straight line, with two carbon–nitrogen triple bonds and two gold–carbon bonds. Enclose the complete structure in brackets with an overall -1 charge.

4.A-2

The given dissolution equation is



Thus each mole of gold requires two moles of cyanide, supplied by two moles of potassium cyanide, $[\text{K}+].[\text{C}-]\# \text{N}$.

Using standard molar masses,

$$M(\text{Au}) = 196.97 \text{ g mol}^{-1}, \quad M(\text{KCN}) = 39.10 + 12.01 + 14.01 = 65.12 \text{ g mol}^{-1}.$$

Hence

$$n(\text{Au}) = \frac{20 \text{ g}}{196.97 \text{ g mol}^{-1}} = 0.10154 \text{ mol},$$

$$n(\text{KCN}) = 2(0.10154) = 0.20308 \text{ mol},$$

and

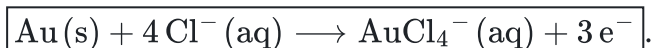
$$m(\text{KCN}) = (0.20308 \text{ mol})(65.12 \text{ g mol}^{-1}) = \boxed{13.2 \text{ g}}.$$

This is the theoretical stoichiometric requirement, approximately 13 g to two significant figures.

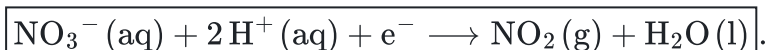
The other molecular or ionic species in the dissolution equation are dioxygen $\text{O}=\text{O}$, water O , and hydroxide $[\text{OH}^-]$.

4.A-3

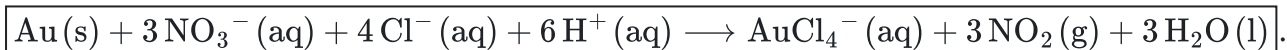
Gold changes from oxidation state 0 to +3, losing three electrons. Including coordination by chloride, the oxidation half-reaction is



Nitrogen changes from +5 in nitrate to +4 in nitrogen dioxide, gaining one electron. Balancing oxygen with water and hydrogen with hydrogen ions gives



Multiplying the reduction half-reaction by three and adding cancels all electrons:



The total charge is -1 on each side, and all atoms balance.

The species are tetrachloridoaurate(III), AuCl_4^- , $[\text{Au}-](\text{Cl})(\text{Cl})(\text{Cl})\text{Cl}$; nitrate, $[\text{O}-][\text{N}+](=\text{O})[\text{O}-]$; chloride, $[\text{Cl}-]$; hydrogen ion, $[\text{H}+]$; nitrogen dioxide, $[\text{O}-][\text{N}+]=\text{O}$; and water, O . The gold complex is square planar. Nitrogen dioxide is a bent radical molecule.

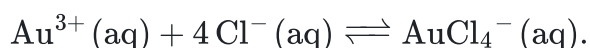
4.A-4

The **oxidizing agent is nitrate**, NO_3^- , $[\text{O}-][\text{N}+](=\text{O})[\text{O}-]$, because it accepts electrons and is reduced: nitrogen changes from +5 to +4.

The **reducing agent is elemental gold**, Au(s) , because it supplies electrons and is oxidized from 0 to +3. Its atomic SMILES is $[\text{Au}]$; this does not represent the extended metallic lattice.

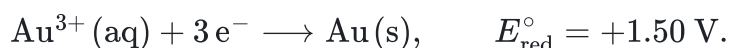
4.A-5

The required formation equilibrium is

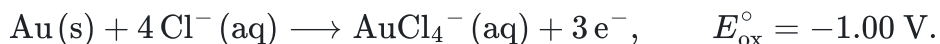


Here the gold(III) ion is $[\text{Au}+3]$, and tetrachloridoaurate(III) is $[\text{Au}-](\text{Cl})(\text{Cl})(\text{Cl})\text{Cl}$.

Use the first given half-reaction in the reduction direction:



Reverse the second half-reaction:



Their sum is the desired formation reaction, with

$$E_{\text{cell}}^{\circ} = 1.50 - 1.00 = 0.50 \text{ V}.$$

Three electrons are transferred in the electrochemical cycle. Therefore,

$$\Delta_r G^{\circ} = -3FE_{\text{cell}}^{\circ} = -RT \ln K,$$

so

$$\ln K = \frac{3FE_{\text{cell}}^{\circ}}{RT}.$$

Using $F = 96485 \text{ C mol}^{-1}$, $R = 8.31446 \text{ J mol}^{-1} \text{ K}^{-1}$, and $T = 298.15 \text{ K}$,

$$\log_{10} K = \frac{3(96485)(0.50)}{(8.31446)(298.15) \ln 10} = 25.355.$$

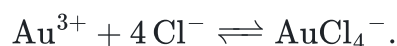
Thus

$$K = 10^{25.355} \approx 2.3 \times 10^{25}.$$

The thermodynamic equilibrium constant is dimensionless; the printed concentration expression implicitly refers concentrations to the standard concentration.

4.A-6

Chloride, $[\text{Cl}^{-}]$, binds gold(III) to form the strongly stabilized tetrachloridoaurate(III) complex:



This greatly decreases the concentration of free gold(III) ions and favors dissolution of gold into the complexed form. Chloride remains in oxidation state -1 .

Therefore the answer is **(c), complexing agent**.

4.B-1

The nanoparticles form by reduction of ionic gold precursors, followed by nucleation and growth into particles containing many gold atoms. The nanostructures are assembled from atomic or molecular starting species.

Therefore this is **(b), a bottom-up approach**.

4.B-2

Trimethyl-n-octylammonium bromide has SMILES CCCCCCC[N+](C)(C)C.[Br-].

Its quaternary ammonium head is charged and hydrophilic, whereas its eight-carbon alkyl chain is hydrophobic and compatible with the organic phase. The ammonium cation can associate with an anion, allowing the resulting ion pair to enter the organic phase.

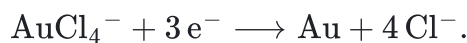
The transferred anion printed in the question is tetrachloridoaluminate(III), AlCl_4^{-} , $[\text{Al}^{-}](\text{Cl})(\text{Cl})(\text{Cl})\text{Cl}$, which has tetrahedral coordination.

The required property is therefore **(b): one side is hydrophilic and the other is hydrophobic**.

4.B-3

Sodium borohydride, NaBH_4 , $[\text{Na}^+] \cdot [\text{BH}_4^-]$, supplies reducing equivalents that convert ionic gold into metallic gold. Its borohydride ion, $[\text{BH}_4^-]$, has tetrahedral geometry.

For the gold(III) precursor, the net gold reduction can be represented as



Therefore sodium borohydride acts as **(a), a reducing agent**.

4.B-4

Approximate both the nanoparticle and an individual gold atom as spheres. Their radii are

$$R = \frac{3 \text{ nm}}{2} = 1.5 \text{ nm}, \quad r = 0.144 \text{ nm}.$$

Ignoring the spaces between packed atoms for this order-of-magnitude estimate,

$$N \approx \frac{V_{\text{particle}}}{V_{\text{atom}}} = \frac{\frac{4}{3}\pi R^3}{\frac{4}{3}\pi r^3} = \left(\frac{R}{r}\right)^3.$$

Thus

$$N \approx \left(\frac{1.5}{0.144}\right)^3 = 1.13 \times 10^3.$$

Accounting for packing voids changes the numerical prefactor but not the order of magnitude. Hence the answer is

$(b), 10^3 \text{ atoms per nanoparticle}$

4.B-5

Approximate the surface atoms as an outer shell **one atomic diameter thick**:

$$t = 2r = 2(0.144) = 0.288 \text{ nm}.$$

The interior radius is then

$$R_{\text{interior}} = R - t = 1.5 - 0.288 = 1.212 \text{ nm}.$$

Using the same average atomic number density in the surface shell and the interior, the fraction of atoms in the shell equals its fraction of the particle volume:

$$f_{\text{surface}} \approx \frac{R^3 - (R - t)^3}{R^3} = 1 - \left(\frac{R - t}{R}\right)^3.$$

Therefore,

$$f_{\text{surface}} \approx 1 - \left(\frac{1.212}{1.5}\right)^3 = 0.4725.$$

Thus approximately 47% of the atoms are in the outer atomic layer, giving

$(b), 40\text{--}50\%$

The solution was checked against the official solution.

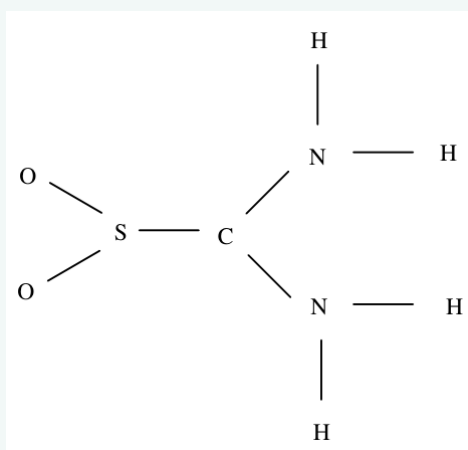
Problem 5: Lewis Structure

5.1 Draw one Lewis structure for each of the following molecules.

- a) N_2
- b) NH_3
- c) O_3
- d) SO_3

5.2 Draw the Lewis structure of carbon monoxide and assign formal charges and oxidation states to both the carbon and oxygen atoms in carbon monoxide.

Thiourea-S,S-dioxide, $\text{O}_2\text{SC}(\text{NH}_2)_2$, has the following skeletal structure



5.3 Draw the Lewis structure of thiourea-S,S-dioxide with zero formal charges on all atoms.

5.4 Based on the Valence Shell Electron Pair Repulsion (VSEPR) model, what is the geometry around the sulfur, carbon, and nitrogen according to the Lewis structure you predicted from 5.3?

5.4a What is the geometry around the sulfur atom? Select your answer from the following choices.

- a) trigonal pyramidal
- b) triangular planar
- c) T-shape

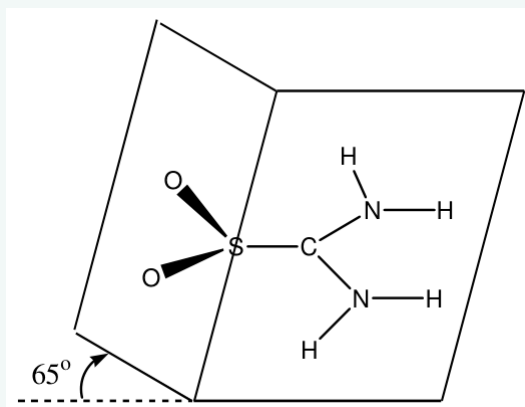
5.4b Similarly, what is the geometry around the C-atom? Select your answer from the following choices.

- a) trigonal pyramidal
- b) triangular planar
- c) T-shape

5.4c Finally, what is the geometry around the N-atom? Select your answer from the following choices.

- a) trigonal pyramidal
- b) triangular planar
- c) T-shape

Molecular structure in the solid state is usually determined by X-ray diffraction analysis. According to this method, the structure of thiourea-S,S-dioxide is shown below:



All the N, H atoms are coplanar with S, C atoms, and the dihedral angle between the OSO plane and the SC(NH₂)₂ plane is 65°.

5.5 Draw the Lewis structure and resonance forms that are consistent with the geometry determined.

Official English text of the problem.

Answers

- **5.1(a):** Dinitrogen, N≡N: an N≡N triple bond and **one lone pair on each N**.
- **5.1(b):** Ammonia, N: three single N–H bonds and **one lone pair on N**.
- **5.1(c):** Ozone, O=[O+][O−]: O=O⁺–O[−]. The double-bonded terminal O, central O, and single-bonded terminal O have **two, one, and three lone pairs**, respectively.
- **5.1(d):** Sulfur trioxide, O=S(=O)=O: three S=O double bonds; **two lone pairs on each O and none on S**. All formal charges are zero.
- **5.2:** Carbon monoxide, [C−]≡[O+]: a triple bond and **one lone pair on each atom**. Formal charges: **C −1, O +1**. Oxidation states: **C +2, O −2**.
- **5.3:** Thiourea-S,S-dioxide, NC(N)=S(=O)=O: O=S(=O)=C(NH₂)₂. Each O has two lone pairs, each N has one, and S and C have none. **Every formal charge is zero**.
- **5.4a: b) triangular planar** around S.
- **5.4b: b) triangular planar** around C.
- **5.4c: a) trigonal pyramidal** around each N.
- **5.5:** Geometry-consistent thiourea-S,S-dioxide contributors include NC(=[NH₂⁺])[S−](=O)=O and [NH₂⁺]=C(N)[S−](=O)=O. Each has a **single S–C bond and one lone pair on S**. Related contributors place the negative formal charge on oxygen, for example NC(=[NH₂⁺])S(=O)[O−]. Together, the resonance description accounts for **pyramidal S and planar C and N environments**.

Solution

For the following electron bookkeeping,

$$\text{formal charge} = V - n_{\text{nonbonding}} - \sum (\text{bond orders}),$$

where V is the number of valence electrons of the neutral atom and $n_{\text{nonbonding}}$ counts nonbonding **electrons**, not pairs.

5.1

a) Dinitrogen, $\text{N}\equiv\text{N}$.

The molecule has $2(5) = 10$ valence electrons. Put six electrons into the triple bond and leave one lone pair on each nitrogen. Both atoms have octets, and each formal charge is

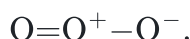
$$5 - 2 - 3 = 0.$$

b) Ammonia, N .

There are $5 + 3(1) = 8$ valence electrons. Three single nitrogen–hydrogen bonds use six electrons; the remaining two constitute a lone pair on nitrogen. Nitrogen has an octet and each hydrogen a duet. All formal charges are zero.

c) Ozone, $\text{O}=[\text{O}^+][\text{O}^-]$.

There are $3(6) = 18$ valence electrons. Draw an O–O–O chain with one double bond and one single bond:



The bonds contain six electrons. Assign two lone pairs to the double-bonded terminal oxygen, one to the central oxygen, and three to the single-bonded terminal oxygen, accounting for the remaining twelve electrons.

The formal charges are

$$\begin{aligned} \text{double-bonded terminal O: } & 6 - 4 - 2 = 0, \\ \text{central O: } & 6 - 2 - 3 = +1, \\ \text{single-bonded terminal O: } & 6 - 6 - 1 = -1. \end{aligned}$$

Exchanging the single and double bonds gives the equivalent resonance contributor.

d) Sulfur trioxide, $\text{O}=\text{S}(=\text{O})=\text{O}$.

There are $6 + 3(6) = 24$ valence electrons. One conventional expanded-octet Lewis structure has three sulfur–oxygen double bonds. These use twelve electrons; the remaining twelve form two lone pairs on each oxygen.

Sulfur has no lone pair and has twelve electrons in its bonding shell. The formal charges are

$$\text{FC}(\text{S}) = 6 - 6 = 0, \quad \text{FC}(\text{O}) = 6 - 4 - 2 = 0.$$

5.2

Carbon monoxide, $[\text{C}^-]\equiv[\text{O}^+]$, has $4 + 6 = 10$ valence electrons. A triple bond and one lone pair on each atom give both atoms octets.

Formal charges follow from equal division of the bonding electrons:

$$\text{FC}(\text{C}) = 4 - 2 - 3 = -1, \quad \text{FC}(\text{O}) = 6 - 2 - 3 = +1.$$

For oxidation states, assign all bonding electrons to the more electronegative oxygen. Carbon retains only its two nonbonding electrons, whereas oxygen receives eight electrons in total:

$$\text{OS}(\text{C}) = 4 - 2 = +2, \quad \text{OS}(\text{O}) = 6 - 8 = -2.$$

Atom	Formal charge	Oxidation state
C	-1	+2
O	+1	-2

5.3

Thiourea-S,S-dioxide has

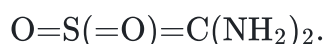
$$2(6) + 6 + 4 + 2(5) + 4(1) = 36$$

valence electrons.

With the specified skeleton and zero formal charges:

- Each nitrogen has three single bonds—two to hydrogen and one to carbon—and one lone pair.
- Each oxygen has a double bond to sulfur and two lone pairs.
- Carbon requires a total bond order of four. Its two single bonds to nitrogen therefore require a double bond to sulfur.

The resulting structure is thiourea-S,S-dioxide, $\text{NC}(\text{N})=\text{S}(=\text{O})=\text{O}$:



Thus, sulfur has three double bonds and no lone pair. The formal-charge check is:

Atom	Nonbonding electrons	Sum of bond orders	Formal charge
S	0	6	$6 - 0 - 6 = 0$
C	0	4	$4 - 0 - 4 = 0$
Each N	2	3	$5 - 2 - 3 = 0$
Each O	4	2	$6 - 4 - 2 = 0$
Each H	0	1	$1 - 0 - 1 = 0$

The structure contains 24 bonding electrons and 12 nonbonding electrons, totaling the required 36.

5.4

In VSEPR, a multiple bond counts as **one electron domain**. Applying the model specifically to the localized, zero-formal-charge structure from 5.3 gives:

Part	Central atom	Bonding domains	Lone pairs	VSEPR type	Predicted geometry and choice
5.4a	S	3	0	AX_3	b) triangular planar
5.4b	C	3	0	AX_3	b) triangular planar
5.4c	Each N	3	1	AX_3E	a) trigonal pyramidal

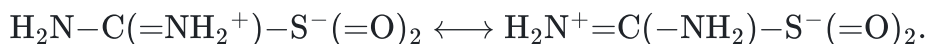
"Triangular planar" in the choices is the usual **trigonal planar** geometry.

5.5

The experimental drawing shows a pyramidal sulfur environment and a planar $\text{SC}(\text{NH}_2)_2$ portion. The zero-formal-charge structure alone does not explain these features.

Starting from that structure, move the carbon–sulfur π -electron pair onto sulfur and donate a nitrogen lone pair into a carbon–nitrogen π bond. This is resonance electron bookkeeping, with no movement of atoms.

A suitable pair of thiourea-S,S-dioxide contributors is:



Their SMILES are NC(=[NH2+])[S-](=O)=O and [NH2+]=C(N)[S-](=O)=O.

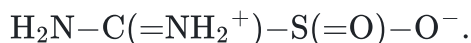
To draw each contributor completely:

- Connect sulfur to carbon by a **single bond**, and to each oxygen by a **double bond**.
- Give sulfur **one lone pair and formal charge -1** .
- Double-bond carbon to one nitrogen. That nitrogen has two N–H bonds, **no lone pair**, and formal charge $+1$.
- Single-bond carbon to the other nitrogen. That nitrogen has two N–H bonds and **one lone pair**.
- Give each oxygen **two lone pairs**.
- Obtain the second contributor by exchanging the roles of the two nitrogen atoms.

The nonzero formal charges are verified by

$$\text{FC}(\text{S}) = 6 - 2 - 5 = -1, \quad \text{FC}(\text{N}_{\text{double-bonded}}) = 5 - 0 - 4 = +1.$$

Related contributors place the negative formal charge on oxygen. One is thiourea-S,S-dioxide, NC(=[NH2+])S(=O)[O-]:



Here sulfur still has **one lone pair**, but its formal charge is zero:

$$\text{FC}(\text{S}) = 6 - 2 - 4 = 0.$$

The single-bonded oxygen has three lone pairs and charge -1 ; the double-bonded oxygen has two lone pairs. Independently exchanging the two nitrogen roles and the two oxygen roles gives **four contributors of this type**.

These resonance descriptions explain the geometry:

- **Sulfur:** three bonded neighbors and one lone pair give an AX_3E , trigonal pyramidal environment.
- **Carbon:** three bonding domains give a trigonal planar environment.
- **Nitrogen:** delocalization across the nitrogen–carbon–nitrogen group gives both carbon–nitrogen bonds partial double-bond character. Planar nitrogen environments permit the required orbital overlap.
- **Relative orientation:** the single carbon–sulfur bond in these contributors accommodates the noncoplanar arrangement shown experimentally. Lewis structures and elementary VSEPR do not determine the numerical dihedral angle of 65° .

The solution was checked against the official solution.

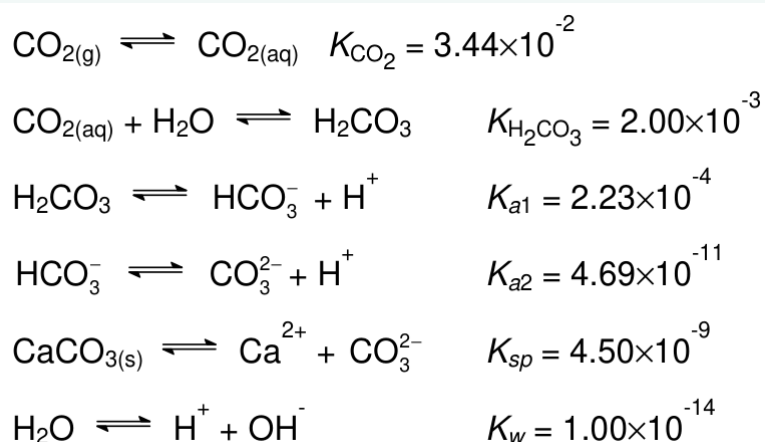
Problem 6: Alkalinity of Water and Solubility of CO₂

Alkalinity of Water and Solubility of CO₂

The capacity of water to accept H⁺ ions is called alkalinity. Alkalinity is important in water treatment and in the chemistry and biology of natural waters. Generally, the basic species responsible for alkalinity in water are HCO₃⁻, CO₃²⁻, and OH⁻. At pH values below 7, H⁺ in water detracts significantly from alkalinity. Therefore, the complete equation for alkalinity in a medium where HCO₃⁻, CO₃²⁻, and OH⁻ are the only contributors to alkalinity can be expressed as

$$\text{alkalinity} = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-] - [\text{H}^+]$$

The contributions made by different species to alkalinity depend upon pH. Relevant chemical equations and equilibrium constants (at 298 K) are shown below:



Note: Calculations must be shown.

6.1 Natural waters (river or lake water) generally contain dissolved CO₂. The ratio of [H₂CO₃] : [HCO₃⁻] : [CO₃²⁻] in a water at [H⁺] = 1.00 × 10⁻⁷ M will be:

$$\underline{(a)} : 1.00 : \underline{(b)}.$$

Calculate (a) and (b).

6.2 Gaseous CO₂ in the atmosphere can be regarded as a contributor to the alkalinity of water in equilibrium with air. Calculate the concentration of CO₂(aq) (mol dm⁻³) in pure water that is in equilibrium with the unpolluted air at 1.01 × 10⁵ Pa and 298 K containing 0.0360 % (molar ratio) CO₂. (assuming standard pressure = 1.01 × 10⁵ Pa).

If you are unable to solve this problem, assume that concentration of CO₂(aq) is equal to 1.11 × 10⁻⁵ M for further calculations.

The solubility (*S*) of CO₂ in water can be defined as

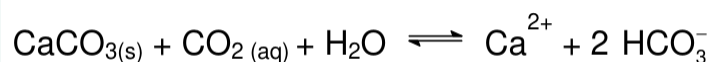
$$S = [\text{CO}_2(\text{aq})] + [\text{H}_2\text{CO}_3] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}].$$

The solubility of atmospheric CO₂ in water that is in equilibrium with the unpolluted air at 298 K and 1.01 × 10⁵ Pa will vary with alkalinity.

6-3 Find the solubility of atmospheric CO_2 in pure water (mol dm^{-3}). Neglect dissociation of water.

6.4 Find the solubility of atmospheric CO_2 (mol dm^{-3}) in a $1.00 \times 10^{-3} \text{ mol dm}^{-3}$ NaOH solution.

At 298 K, $1.01 \times 10^5 \text{ Pa}$ unpolluted air is in equilibrium with natural water saturated with CaCO_3 . The following main equilibrium may exist:



6.5 Calculate the equilibrium constant for the above equation.

If you are unable to solve this problem, assume that equilibrium constant $K_{\text{eq}} = 5.00 \times 10^{-5}$ for further calculations.

6.6 Calculate the concentration of Ca^{2+} (mg dm^{-3}) in CaCO_3 -saturated natural water that is in equilibrium with atmospheric CO_2 .

If you are unable to solve this problem, assume that concentration of $\text{Ca}^{2+}(\text{aq}) = 40.1 \text{ mg dm}^{-3}$ for further calculations.

6.7 Find the alkalinity (mol/L) of the above solution.

6.8 In an underground lake saturated with CaCO_3 , the water has a high content of CO_2 . The concentration of Ca^{2+} in this lake was found to be as high as 100 mg dm^{-3} . Assume the lake and the air above is a closed system, calculate the effective pressure of CO_2 (Pa) in air which is in equilibrium with this Ca^{2+} content.

Official English text of the problem.

Answers

The results retain all given equilibria, except water dissociation in **6-3**, as instructed. Parenthetical alternatives use the approximation $[\text{HCO}_3^-] \approx 2[\text{Ca}^{2+}]$.

- **6.1:** $a = 4.48 \times 10^{-4}$, $b = 4.69 \times 10^{-4}$; hence the ratio is $4.48 \times 10^{-4} : 1.00 : 4.69 \times 10^{-4}$.
- **6.2:** $[\text{CO}_2(\text{aq})] = 1.24 \times 10^{-5} \text{ mol dm}^{-3}$.
- **6-3:** $S = 1.48 \times 10^{-5} \text{ mol dm}^{-3}$.
- **6.4:** $S = 1.00 \times 10^{-3} \text{ mol dm}^{-3}$.
- **6.5:** $K_{\text{eq}} = 4.28 \times 10^{-5}$.
- **6.6:** $[\text{Ca}^{2+}] = 20.7 \text{ mg dm}^{-3}$ (20.4 mg dm^{-3} with the approximation).
- **6.7:** Alkalinity = $1.03 \times 10^{-3} \text{ mol L}^{-1}$ ($1.02 \times 10^{-3} \text{ mol L}^{-1}$ with the approximation).
- **6.8:** $p_{\text{CO}_2} = 4.25 \times 10^3 \text{ Pa}$ ($4.26 \times 10^3 \text{ Pa}$ with the approximation).

Solution

The species used below have the following names and SMILES:

Species and name	SMILES
CO ₂ , carbon dioxide	O=C=O
H ₂ O, water	O
H ₂ CO ₃ , carbonic acid	O=C(O)O
HCO ₃ ⁻ , hydrogen carbonate (bicarbonate) ion	O=C(O)[O-]
CO ₃ ²⁻ , carbonate ion	O=C([O-])[O-]
H ⁺ , hydrogen ion (proton)	[H+]
OH ⁻ , hydroxide ion	[OH-]
Ca ²⁺ , calcium ion	[Ca+2]
Na ⁺ , sodium ion	[Na+]
CaCO ₃ , calcium carbonate	[Ca+2].[O-]C(=O)[O-]
NaOH, sodium hydroxide	[Na+].[OH-]

The disconnected-ion SMILES for the salts do not describe their crystal lattices. SMILES also do not specify gas versus aqueous state or aqueous solvation; H⁺ is the conventional shorthand for the solvated proton.

Use ideal-solution equilibrium expressions, with concentrations in mol dm⁻³ and unit standard concentration understood. Pure water and solid calcium carbonate have unit activity. For mass conversions, take $M(\text{Ca}) = 40.1 \text{ g mol}^{-1}$.

6.1

The two acid dissociations give

$$K_{a1} = \frac{[\text{HCO}_3^-][\text{H}^+]}{[\text{H}_2\text{CO}_3]}, \quad K_{a2} = \frac{[\text{CO}_3^{2-}][\text{H}^+]}{[\text{HCO}_3^-]}.$$

Normalizing the bicarbonate concentration to 1.00,

$$a = \frac{[\text{H}_2\text{CO}_3]}{[\text{HCO}_3^-]} = \frac{1.00 \times 10^{-7}}{2.23 \times 10^{-4}} = \boxed{4.48 \times 10^{-4}},$$

$$b = \frac{[\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} = \frac{4.69 \times 10^{-11}}{1.00 \times 10^{-7}} = \boxed{4.69 \times 10^{-4}}.$$

Thus bicarbonate overwhelmingly predominates among these three species at the specified hydrogen-ion concentration.

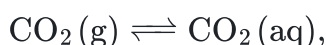
6.2

The carbon dioxide mole fraction and partial pressure are

$$y_{\text{CO}_2} = \frac{0.0360}{100} = 3.60 \times 10^{-4},$$

$$p_{\text{CO}_2} = y_{\text{CO}_2}P = (3.60 \times 10^{-4})(1.01 \times 10^5) = 36.36 \text{ Pa}.$$

For



the given equilibrium constant uses pressure relative to the standard pressure:

$$K_{\text{CO}_2} = \frac{[\text{CO}_2(\text{aq})]/c^\circ}{p_{\text{CO}_2}/p^\circ}, \quad c^\circ = 1 \text{ mol dm}^{-3}.$$

Therefore,

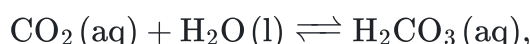
$$[\text{CO}_2(\text{aq})] = (3.44 \times 10^{-2}) \frac{36.36}{1.01 \times 10^5} (1 \text{ mol dm}^{-3}) = 1.2384 \times 10^{-5} \text{ mol dm}^{-3}.$$

$$\boxed{[\text{CO}_2(\text{aq})] = 1.24 \times 10^{-5} \text{ mol dm}^{-3}}$$

This is the concentration of molecular dissolved carbon dioxide, rather than the sum of all dissolved carbon species.

6-3

Hydration gives



so

$$[\text{H}_2\text{CO}_3] = K_{\text{H}_2\text{CO}_3}[\text{CO}_2(\text{aq})] = (2.00 \times 10^{-3})(1.2384 \times 10^{-5}) = 2.4768 \times 10^{-8} \text{ M}.$$

Define

$$h = [\text{H}^+], \quad A = K_{a1}[\text{H}_2\text{CO}_3] = 5.523264 \times 10^{-12} \text{ M}^2.$$

Then

$$[\text{HCO}_3^-] = \frac{A}{h}, \quad [\text{CO}_3^{2-}] = \frac{K_{a2}A}{h^2}.$$

Neglecting water dissociation, electroneutrality requires

$$h = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] = \frac{A}{h} + \frac{2K_{a2}A}{h^2}.$$

The second dissociation is very small, so initially

$$h \simeq \sqrt{A} = 2.3502 \times 10^{-6} \text{ M}.$$

Indeed,

$$\frac{[\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} = \frac{K_{a2}}{h} \simeq 2.00 \times 10^{-5},$$

which verifies that approximation. Retaining the small carbonate term gives

$$[\text{HCO}_3^-] = 2.35012 \times 10^{-6} \text{ M}, \quad [\text{CO}_3^{2-}] = 4.68981 \times 10^{-11} \text{ M}.$$

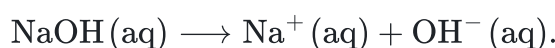
Hence

$$\begin{aligned} S &= 1.2384 \times 10^{-5} + 2.4768 \times 10^{-8} + 2.35012 \times 10^{-6} + 4.68981 \times 10^{-11} \\ &= 1.47589 \times 10^{-5} \text{ mol dm}^{-3}. \end{aligned}$$

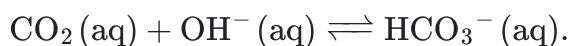
$$\boxed{S = 1.48 \times 10^{-5} \text{ mol dm}^{-3}}$$

6.4

Sodium hydroxide dissociates completely:



Atmospheric carbon dioxide consumes hydroxide, principally through



Consequently, the final hydroxide concentration is not the initial analytical sodium hydroxide concentration. The conserved sodium concentration is

$$[\text{Na}^+] = 1.00 \times 10^{-3} \text{ M}.$$

Equilibrium with the same atmosphere fixes $[\text{CO}_2(\text{aq})]$, $[\text{H}_2\text{CO}_3]$, and A at the values found above. Electroneutrality gives

$$[\text{Na}^+] + h = \frac{A}{h} + \frac{2K_{a2}A}{h^2} + \frac{K_w}{h}.$$

Thus

$$1.00 \times 10^{-3} = \frac{A + K_w}{h} + \frac{2K_{a2}A}{h^2} - h.$$

Equivalently,

$$h^3 + (1.00 \times 10^{-3})h^2 - (A + K_w)h - 2K_{a2}A = 0.$$

The positive root is

$$h = 5.62533 \times 10^{-9} \text{ M},$$

giving

$$\begin{aligned} &= 9.81856 \times 10^{-4} \text{ M}, \\ [\text{CO}_3^{2-}] &= 8.18602 \times 10^{-6} \text{ M}, \\ [\text{OH}^-] &= 1.77767 \times 10^{-6} \text{ M}. \end{aligned}$$

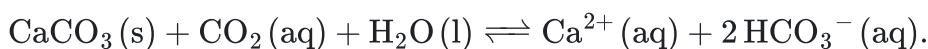
Therefore,

$$\begin{aligned} S &= 1.2384 \times 10^{-5} + 2.4768 \times 10^{-8} + 9.81856 \times 10^{-4} + 8.18602 \times 10^{-6} \\ &= 1.00245 \times 10^{-3} \text{ mol dm}^{-3}. \end{aligned}$$

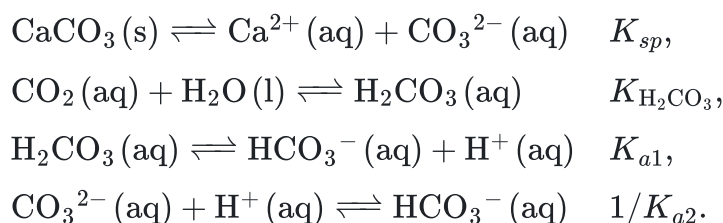
$$\boxed{S = 1.00 \times 10^{-3} \text{ mol dm}^{-3}}$$

6.5

The required balanced reaction is



It is obtained by adding the following equilibria:



Adding reactions multiplies their equilibrium constants, so

$$K_{\text{eq}} = \frac{K_{sp}K_{\text{H}_2\text{CO}_3}K_{a1}}{K_{a2}} = \frac{(4.50 \times 10^{-9})(2.00 \times 10^{-3})(2.23 \times 10^{-4})}{4.69 \times 10^{-11}}.$$

$$\boxed{K_{\text{eq}} = 4.28 \times 10^{-5}}$$

Its activity expression is

$$K_{\text{eq}} = \frac{a_{\text{Ca}^{2+}} a_{\text{HCO}_3^-}^2}{a_{\text{CO}_2(\text{aq})}}.$$

With the concentration convention used here, its working expression is

$$K_{\text{eq}} = \frac{[\text{Ca}^{2+}][\text{HCO}_3^-]^2}{[\text{CO}_2(\text{aq})]}.$$

6.6

Write $x = [\text{Ca}^{2+}]$. If bicarbonate is the dominant anion, electroneutrality gives

$$[\text{HCO}_3^-] \simeq 2x.$$

The main equilibrium then yields

$$K_{\text{eq}} \simeq \frac{x(2x)^2}{[\text{CO}_2(\text{aq})]},$$

so

$$x \simeq \left(\frac{K_{\text{eq}}[\text{CO}_2(\text{aq})]}{4} \right)^{1/3} = \left(\frac{(4.27932 \times 10^{-5})(1.2384 \times 10^{-5})}{4} \right)^{1/3} = 5.09791 \times 10^{-4} \text{ M}.$$

This approximation gives

$$[\text{Ca}^{2+}] \simeq (5.09791 \times 10^{-4})(40.1)(10^3) = \boxed{20.4 \text{ mg dm}^{-3}}.$$

To retain all the supplied equilibria, use the complete charge balance

$$2x + h = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-],$$

together with

$$[\text{HCO}_3^-] = \frac{A}{h}, \quad [\text{CO}_3^{2-}] = \frac{K_{a2}A}{h^2}, \quad x = \frac{K_{sp}h^2}{K_{a2}A}.$$

Substitution gives a single equation:

$$\frac{2K_{sp}h^2}{K_{a2}A} + h = \frac{A + K_w}{h} + \frac{2K_{a2}A}{h^2}.$$

Its positive solution is

$$h = 5.45130 \times 10^{-9} \text{ M}, \quad x = 5.16232 \times 10^{-4} \text{ M}.$$

The corresponding anion concentrations are

$$\begin{aligned} &= 1.01320 \times 10^{-3} \text{ M}, \\ [\text{CO}_3^{2-}] &= 8.71702 \times 10^{-6} \text{ M}, \\ [\text{OH}^-] &= 1.83442 \times 10^{-6} \text{ M}. \end{aligned}$$

Thus the complete equilibrium calculation gives

$$\boxed{[\text{Ca}^{2+}] = (5.16232 \times 10^{-4})(40.1)(10^3) = 20.7 \text{ mg dm}^{-3}}.$$

The dominant-bicarbonate approximation underestimates this result by about 1.25%.

6.7

Rearranging the charge balance from 6.6,

$$[\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-] - [\text{H}^+] = 2[\text{Ca}^{2+}].$$

Therefore, for the specified calcium carbonate–carbon dioxide–water system,

$$\text{alkalinity} = 2[\text{Ca}^{2+}].$$

Using the complete equilibrium result,

$$\text{alkalinity} = 2(5.16232 \times 10^{-4}) = 1.03246 \times 10^{-3} \text{ mol L}^{-1},$$

$$\boxed{\text{alkalinity} = 1.03 \times 10^{-3} \text{ mol L}^{-1}}.$$

Using the approximate calcium concentration instead gives

$$\boxed{\text{alkalinity} \simeq 1.02 \times 10^{-3} \text{ mol L}^{-1}}.$$

6.8

Convert the measured calcium concentration:

$$x = [\text{Ca}^{2+}] = \frac{100 \times 10^{-3} \text{ g dm}^{-3}}{40.1 \text{ g mol}^{-1}} = 2.49377 \times 10^{-3} \text{ M}.$$

Calcium carbonate saturation fixes the carbonate concentration:

$$D = [\text{CO}_3^{2-}] = \frac{K_{sp}}{x} = \frac{4.50 \times 10^{-9}}{2.49377 \times 10^{-3}} = 1.80450 \times 10^{-6} \text{ M}.$$

From the second acid dissociation,

$$[\text{HCO}_3^-] = \frac{Dh}{K_{a2}}.$$

The complete charge balance is consequently

$$2x + h = \frac{Dh}{K_{a2}} + 2D + \frac{K_w}{h},$$

or

$$\left(\frac{D}{K_{a2}} - 1 \right) h^2 - (2x - 2D)h + K_w = 0.$$

The root corresponding to the high- CO_2 water specified in the question gives

$$h = 1.29536 \times 10^{-7} \text{ M}, \quad [\text{HCO}_3^-] = 4.98397 \times 10^{-3} \text{ M}.$$

The equilibrium from 6.5 now determines molecular dissolved carbon dioxide:

$$[\text{CO}_2(\text{aq})] = \frac{x[\text{HCO}_3^-]^2}{K_{\text{eq}}} = \frac{(2.49377 \times 10^{-3})(4.98397 \times 10^{-3})^2}{4.27932 \times 10^{-5}} = 1.44755 \times 10^{-3} \text{ M}.$$

Applying Henry's law,

$$p_{\text{CO}_2} = p^\circ \frac{[\text{CO}_2(\text{aq})]/c^\circ}{K_{\text{CO}_2}} = (1.01 \times 10^5) \frac{1.44755 \times 10^{-3}}{3.44 \times 10^{-2}} = 4.25007 \times 10^3 \text{ Pa}.$$

$$\boxed{p_{\text{CO}_2} = 4.25 \times 10^3 \text{ Pa}}$$

With the simpler approximation $[\text{HCO}_3^-] \simeq 2x$,

$$p_{\text{CO}_2} \simeq p^\circ \frac{4x^3}{K_{\text{eq}}K_{\text{CO}_2}} = \boxed{4.26 \times 10^3 \text{ Pa}}.$$

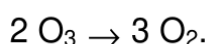
The headspace volume is unnecessary: the aqueous equilibrium composition determines the required equilibrium partial pressure.

The solution was checked against the official solution.

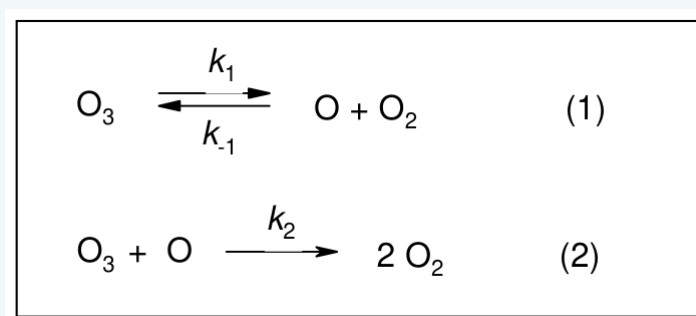
Problem 7: Kinetic Behaviour of Ozone

Ozone (O_3) is a form of oxygen. It is a natural component of the stratosphere, where it shields the earth from life-destroying ultraviolet radiation. On absorbing light in this region, ozone is converted to dioxygen molecules.

For the overall reaction of ozone decomposition,



One of the proposed mechanisms is expressed as



where k_1 , k_{-1} , and k_2 are the rate constants.

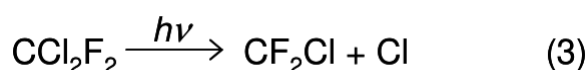
7.1 According to the above mechanism what are the differential rate equations for the formation (or consumption) of O_3 , O_2 , and O at time t , assuming step 2 is irreversible.

7.2 Simplification in obtaining the rate law may be found by making appropriate assumptions. Assuming that the concentration of O atoms reaches equilibrium rapidly, its concentration may be given by the equilibrium constant of the reaction (1). The second step is rate determining. Under this equilibrium approximation, deduce the differential rate equation for the O_3 depletion as a function of O_2 and O_3 concentrations.

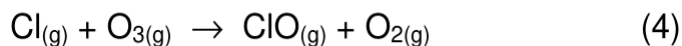
7.3 Another assumption frequently made is that the rates of oxygen atom production and consumption are equal (this is called steady state). Under the steady state approximation, that is $d[\text{O}]/dt = 0$, show that the rate equation is:

$$-\frac{d[\text{O}_3]}{dt} = \frac{2k_1k_2[\text{O}_3]^2}{k_{-1}[\text{O}_2] + k_2[\text{O}_3]}.$$

One pathway for the destruction of ozone ($2 \text{O}_3 \rightarrow 3 \text{O}_2$) in the upper atmosphere is catalyzed by Freons. For instance, when CCl_2F_2 (Freon-12) migrates to the upper atmosphere, the ultraviolet photolysis of CCl_2F_2 may give rise to Cl atoms according to the following reaction:



7.4 Chlorine atom can act as a catalyst for the destruction of ozone. The first slow step of a Cl-catalyzed mechanism is proposed as follows:



Assuming a two-step mechanism, propose the second step in the mechanism.

7.5 The activation energy for Cl-catalyzed destruction of ozone is 2.1 kJ mol^{-1} , while the activation energy for the reaction without the presence of catalyst is 14.0 kJ mol^{-1} . Estimate the ratio of the rate constant for the catalyzed reaction to that for the uncatalyzed reaction at 25°C . Assume the frequency factor is the same for each reaction.

Official English text of the problem.

Answers

- **7.1**

$$\begin{aligned} \frac{d[\text{O}_3]}{dt} &= -k_1[\text{O}_3] + k_{-1}[\text{O}][\text{O}_2] - k_2[\text{O}_3][\text{O}], \\ \frac{d[\text{O}_2]}{dt} &= k_1[\text{O}_3] - k_{-1}[\text{O}][\text{O}_2] + 2k_2[\text{O}_3][\text{O}], \\ \frac{d[\text{O}]}{dt} &= k_1[\text{O}_3] - k_{-1}[\text{O}][\text{O}_2] - k_2[\text{O}_3][\text{O}]. \end{aligned}$$

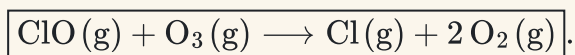
- **7.2** With literal cancellation of the forward and reverse equilibrium rates,

$$-\frac{d[\text{O}_3]}{dt} = \frac{k_1 k_2}{k_{-1}} \frac{[\text{O}_3]^2}{[\text{O}_2]}.$$

- **7.3**

$$-\frac{d[\text{O}_3]}{dt} = \frac{2k_1 k_2 [\text{O}_3]^2}{k_{-1} [\text{O}_2] + k_2 [\text{O}_3]}.$$

- **7.4**



- **7.5**

$$\frac{k_{\text{cat}}}{k_{\text{uncat}}} \approx 1.2 \times 10^2$$

—a dimensionless ratio of approximately 120.

Solution

The species appearing in the mechanism are identified below.

Formula	Name	SMILES
O ₃	Ozone	O=[O+][O-]
O ₂	Dioxygen	O=O
O	Oxygen atom	[O]
Cl	Chlorine atom	[Cl]
ClO	Chlorine monoxide radical	Cl[O]
CCl ₂ F ₂	Dichlorodifluoromethane (Freon-12)	FC(F)(Cl)Cl
CF ₂ Cl	Chlorodifluoromethyl radical	F[C](F)Cl

The ozone SMILES depicts one resonance contributor; the actual molecule is bent with equivalent oxygen–oxygen bonds. These SMILES do not specify electronic spin states, including the triplet ground state of dioxygen. The photolysis shown in reaction (3) involves homolytic carbon–chlorine bond cleavage, with one bonding electron going to each radical fragment.

7.1

For the elementary reactions



define the event rates

$$v_1 = k_1[\text{O}_3], \quad v_{-1} = k_{-1}[\text{O}][\text{O}_2], \quad v_2 = k_2[\text{O}_3][\text{O}].$$

Each forward event of step (1) consumes one ozone molecule and produces one oxygen atom and one dioxygen molecule. The reverse event has the opposite effects. Each event of step (2) consumes one ozone molecule and one oxygen atom and produces two dioxygen molecules. Therefore,

$$\begin{aligned} \frac{d[\text{O}_3]}{dt} &= -v_1 + v_{-1} - v_2, \\ \frac{d[\text{O}_2]}{dt} &= v_1 - v_{-1} + 2v_2, \\ \frac{d[\text{O}]}{dt} &= v_1 - v_{-1} - v_2. \end{aligned}$$

Substitution gives the three expanded equations in the answers.

As an atom-balance check,

$$\frac{d}{dt}(3[\text{O}_3] + 2[\text{O}_2] + [\text{O}]) = 0.$$

If concentrations are expressed in mol L⁻¹, k_1 has units s⁻¹, while k_{-1} and k_2 have units L mol⁻¹ s⁻¹.

7.2

For equilibrium in step (1),

$$k_1[\text{O}_3] = k_{-1}[\text{O}][\text{O}_2],$$

so

$$K_c = \frac{[\text{O}][\text{O}_2]}{[\text{O}_3]} = \frac{k_1}{k_{-1}}, \quad [\text{O}]_{\text{eq}} = \frac{k_1[\text{O}_3]}{k_{-1}[\text{O}_2]}.$$

Applying the literal equilibrium cancellation $v_1 = v_{-1}$ to the ozone balance in 7.1 gives

$$-\frac{d[\text{O}_3]}{dt} = v_2 = k_2[\text{O}_3][\text{O}]_{\text{eq}}.$$

Hence,

$$\boxed{-\frac{d[\text{O}_3]}{dt} = \frac{k_1 k_2 [\text{O}_3]^2}{k_{-1} [\text{O}_2]}.$$

This expression is second order in ozone and inverse first order in dioxygen. The equilibrium cancellation used here differs from the steady-state condition imposed next.

7.3

The steady-state condition for oxygen atoms is

$$0 = \frac{d[\text{O}]}{dt} = k_1[\text{O}_3] - (k_{-1}[\text{O}_2] + k_2[\text{O}_3])[\text{O}].$$

Consequently,

$$[\text{O}]_{\text{ss}} = \frac{k_1[\text{O}_3]}{k_{-1}[\text{O}_2] + k_2[\text{O}_3]}.$$

The same condition can be written

$$v_1 - v_{-1} = v_2.$$

Substituting this into the ozone balance,

$$-\frac{d[\text{O}_3]}{dt} = v_1 - v_{-1} + v_2 = 2v_2.$$

Thus,

$$\boxed{-\frac{d[\text{O}_3]}{dt} = 2k_2[\text{O}_3][\text{O}]_{\text{ss}} = \frac{2k_1 k_2 [\text{O}_3]^2}{k_{-1}[\text{O}_2] + k_2[\text{O}_3]}.$$

The factor of two has a stoichiometric origin: step (2) consumes one ozone molecule, while net forward reaction through step (1) consumes another ozone molecule to replace the oxygen atom used in step (2).

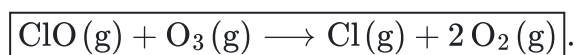
7.4

The second step must consume the chlorine monoxide intermediate, regenerate the chlorine catalyst, and complete the overall reaction $2 \text{O}_3 \longrightarrow 3 \text{O}_2$.

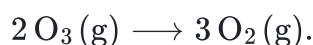
Subtracting the given first step,



from the required overall reaction gives



Adding these two steps cancels both Cl and ClO, leaving



The proposed step conserves one chlorine atom and four oxygen atoms. Chlorine is regenerated and is therefore the catalyst; chlorine monoxide is formed and subsequently consumed and is therefore an intermediate.

7.5

The Arrhenius equation is

$$k = A \exp \left(-\frac{E_a}{RT} \right).$$

Because the frequency factors are assumed equal,

$$\frac{k_{\text{cat}}}{k_{\text{uncat}}} = \exp \left(\frac{E_{a,\text{uncat}} - E_{a,\text{cat}}}{RT} \right).$$

The activation-energy difference and temperature are

$$\begin{aligned} \Delta E_a &= (14.0 - 2.1) \text{ kJ mol}^{-1} = 11900 \text{ J mol}^{-1}, \\ T &= 25 + 273.15 = 298.15 \text{ K}. \end{aligned}$$

Using $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$,

$$\frac{k_{\text{cat}}}{k_{\text{uncat}}} = \exp \left[\frac{11900 \text{ J mol}^{-1}}{(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(298.15 \text{ K})} \right] = e^{4.8007} = 121.6.$$

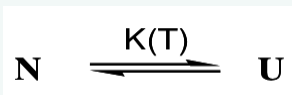
Therefore,

$$\boxed{\frac{k_{\text{cat}}}{k_{\text{uncat}}} \approx 1.2 \times 10^2}.$$

The solution was checked against the official solution.

Problem 8: Protein Folding

Most proteins exist usually only in two forms, the native form (N) and the unfolded form (U) when they are thermally or chemically denatured, without appreciable concentrations of other stable intermediates in equilibrium with the native and unfolded forms. For these proteins, the folding-unfolding equilibrium can be described by the following simple chemical equation:



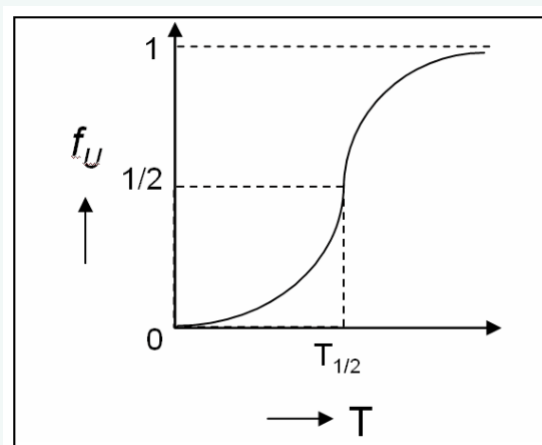
where N and U denote the folded state (native state) and the unfolded state (denatured state) of the protein, respectively. $K(T)$ is the equilibrium constant for the process at absolute temperature T .

8.1 What is the equilibrium constant for the process when the native and denatured states are present in equal proportions at equilibrium?

8.2 What is the standard free energy change of the process ($\Delta G^\circ(T)$) when the native and denatured states are present in equal proportions at equilibrium? Express your answer in SI units.

8.3 If $(C_N)_{\text{eq}}$ and $(C_U)_{\text{eq}}$ denote the equilibrium concentrations of N and U in solution, respectively, and C is the total concentration of the protein, the fraction of the total protein that is unfolded under the equilibrium condition is given by $f_U = (C_U)_{\text{eq}}/C$. Deduce an expression for f_U in terms of the equilibrium constant K . Show all work on the answer sheet.

When a protein is denatured by increasing the temperature of the solution, the fraction of the unfolded protein increases with temperature, as shown in the following Figure.



The mid-point of the denaturation curve is given by $f_U = \frac{1}{2}$ and $T = T_{1/2}$. The latter is often referred to as the denaturation temperature. At temperatures higher than $T_{1/2}$, f_U increases above $\frac{1}{2}$, but at temperatures lower than $T_{1/2}$, f_U decreases below $\frac{1}{2}$.

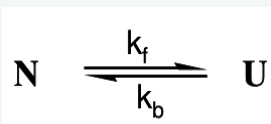
8.4 What is the sign of $\Delta G^\circ(T)$ at temperatures below and above $T_{1/2}$? Select your answer from the following choices.

- a) Negative both below and above $T_{1/2}$.
- b) Positive both below and above $T_{1/2}$.
- c) Positive below $T_{1/2}$, but negative above $T_{1/2}$.
- d) Negative below $T_{1/2}$, but positive above $T_{1/2}$.

8.5 How does the standard Gibbs free energy change for the process vary when the temperature (i) increases above $T_{1/2}$ and (ii) decreases below $T_{1/2}$? Select your answer from the following choices.

- a) Decrease in both cases.
- b) Increase in both cases.
- c) Increases above $T_{1/2}$, but decreases below $T_{1/2}$.
- d) Decreases above $T_{1/2}$, but increases below $T_{1/2}$.

The kinetics of unfolding and refolding of a protein has recently become an intense area of study. We could rewrite the chemical equation for the process as follows:



where k_f and k_b denote the forward and backward reaction rate constants, respectively, assuming that both the forward and reverse processes are elementary steps that follow first-order kinetics.

8.6 For the simple chemical equation and elementary kinetic steps used to describe the protein folding-unfolding process outlined above, what is the relationship between equilibrium constant K and the rate constants k_f and k_b ?

8.7 Derive a rate law for the overall process, that is dC_U/dt in terms of only rate constants, C_U and $(C_U)_{eq}$.

Official English text of the problem.

Answers

- **8.1:** $K = 1$, dimensionless.
- **8.2:** $\Delta G^\circ(T) = 0 \text{ J mol}^{-1}$.
- **8.3:** $f_U = \frac{K}{1 + K}$.
- **8.4:** (c) — positive below $T_{1/2}$, negative above $T_{1/2}$.
- **8.5:** (d) — relative to its value at $T_{1/2}$, ΔG° decreases on heating above the midpoint and increases on cooling below it.
- **8.6:** $K = \frac{k_f}{k_b}$.
- **8.7:** $\frac{dC_U}{dt} = (k_f + k_b)[(C_U)_{eq} - C_U]$.

Solution

Throughout, the forward process is unfolding, $N \longrightarrow U$. The labels denote the native and unfolded conformations of the same protein. Its molecular structure is unspecified, so no unique SMILES can be assigned; ordinary SMILES also does not describe the folding conformation.

8.1

For the two-state equilibrium $N \rightleftharpoons U$, the equilibrium constant in the concentration model used here is

$$K(T) = \frac{(C_U)_{eq}}{(C_N)_{eq}}.$$

Equal proportions mean equal concentrations, giving

$$K(T) = 1.$$

The ratio, and hence K , is dimensionless.

8.2

The standard reaction Gibbs energy and equilibrium constant satisfy

$$\Delta G^\circ(T) = -RT \ln K(T).$$

Using $K = 1$,

$$\boxed{\Delta G^\circ(T) = -RT \ln 1 = 0 \text{ J mol}^{-1}}.$$

8.3

Conservation of the total protein concentration gives

$$C = (C_N)_{\text{eq}} + (C_U)_{\text{eq}}.$$

Since

$$(C_U)_{\text{eq}} = K(C_N)_{\text{eq}},$$

the unfolded fraction is

$$\begin{aligned} f_U &= \frac{(C_U)_{\text{eq}}}{(C_N)_{\text{eq}} + (C_U)_{\text{eq}}} \\ &= \frac{K(C_N)_{\text{eq}}}{(1 + K)(C_N)_{\text{eq}}} \\ &= \boxed{\frac{K}{1 + K}}. \end{aligned}$$

Equivalently,

$$K = \frac{f_U}{1 - f_U}.$$

8.4

Below the denaturation midpoint,

$$f_U < \frac{1}{2} \implies K = \frac{f_U}{1 - f_U} < 1.$$

Thus $\ln K < 0$, and because $R, T > 0$,

$$\Delta G^\circ(T) = -RT \ln K > 0.$$

Above the midpoint,

$$f_U > \frac{1}{2} \implies K > 1 \implies \Delta G^\circ(T) < 0.$$

Therefore the answer is **(c)**:

$$\boxed{\begin{cases} \Delta G^\circ(T) > 0, & T < T_{1/2}, \\ \Delta G^\circ(T) = 0, & T = T_{1/2}, \\ \Delta G^\circ(T) < 0, & T > T_{1/2}. \end{cases}}$$

8.5

At $T_{1/2}$, equal populations give $K = 1$ and $\Delta G^\circ = 0$.

(i) Heating above $T_{1/2}$ increases the unfolded fraction, giving $K > 1$. Consequently, $\Delta G^\circ = -RT \ln K$ becomes negative: it **decreases from its midpoint value**.

(ii) Cooling below $T_{1/2}$ decreases the unfolded fraction, giving $K < 1$. Consequently, ΔG° becomes positive: it **increases from its midpoint value**.

Thus the intended choice is

$$\boxed{(d)}.$$

8.6

The first-order forward and backward reaction rates are

$$r_f = k_f C_N, \quad r_b = k_b C_U.$$

At equilibrium these rates are equal:

$$k_f (C_N)_{\text{eq}} = k_b (C_U)_{\text{eq}}.$$

Rearranging,

$$\boxed{K = \frac{(C_U)_{\text{eq}}}{(C_N)_{\text{eq}}} = \frac{k_f}{k_b}}.$$

Both first-order rate constants have SI units s^{-1} , so their ratio is dimensionless.

8.7

At fixed temperature, the net rate of formation of unfolded protein is

$$\frac{dC_U}{dt} = k_f C_N - k_b C_U.$$

The total protein concentration is conserved:

$$C_N + C_U = C.$$

Substituting $C_N = C - C_U$,

$$\frac{dC_U}{dt} = k_f C - (k_f + k_b) C_U.$$

At equilibrium, the derivative vanishes, so

$$k_f C = (k_f + k_b) (C_U)_{\text{eq}}.$$

Eliminating C yields the requested rate law:

$$\boxed{\frac{dC_U}{dt} = (k_f + k_b) [(C_U)_{\text{eq}} - C_U]}.$$

This correctly predicts an increase in C_U when it is below equilibrium and a decrease when it is above equilibrium. With concentrations in mol m^{-3} , the rate has units $\text{mol m}^{-3} \text{s}^{-1}$.

The solution was checked against the official solution.