

IChO 1984

Theory problems and solutions · Frankfurt am Main, German Federal Republic · 8 theory problems with complete solutions

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Problem 1: Radioactive dating with ^{14}C and $^{87}\text{Rb}/^{87}\text{Sr}$

A)

The element carbon consists of the stable isotopes ^{12}C (98.90 percent of atoms) and ^{13}C (1.10 percent of atoms). In addition, carbon contains a small fraction of the radioisotope ^{14}C ($t_{1/2} = 5730$ years), which is continuously formed in the atmosphere by cosmic rays as CO_2 . ^{14}C mixes with the isotopes ^{12}C and ^{13}C via the natural CO_2 cycle.

The decay rate of ^{14}C is described by (N = number of ^{14}C atoms; t = time; λ = decay constant):

$$\text{decay rate} = -\frac{dN}{dt} = \lambda N \quad (1)$$

Integration of (1) leads to the well-known rate law (2) for the radioactive decay:

$$N = N_0 e^{-\lambda t} \quad (2)$$

N_0 = number of ^{14}C atoms at $t = 0$

1.1 What is the mathematical relationship between the parameters α and $t_{1/2}$ (= half life)?

1.2 The decay rate of carbon, which is a part of the natural CO_2 cycle, is found to be 13.6 disintegrations per minute and gram of carbon. When a plant (e. g. a tree) dies, it no longer takes part in the CO_2 cycle. As a consequence, the decay rate of carbon decreases.

In 1983, a decay rate of 12.0 disintegrations per minute and gram of carbon was measured for a piece of wood which belongs to a ship of the Vikings. In which year was cut the tree from which this piece of wood originated?

1.3 Assume that the error of the decay rate of 12.0 disintegrations per minute and gram of carbon is 0.2 disintegrations per minute and gram of carbon. What is the corresponding error in the age of the wood in question b)?

1.4 What is the isotope $^{12}\text{C}/^{14}\text{C}$ ratio of carbon, which takes part in the natural CO_2 cycle (1 year = 365 days)?

B)

The elements strontium and rubidium have the following isotope composition:

Strontium: 0.56 % ^{84}Sr ; 9.86 % ^{86}Sr ; 7.00 % ^{87}Sr ; 82.58 % ^{88}Sr (these isotopes are all stable).

Rubidium: 72.17 % ^{85}Rb (stable) ; 27.83 % ^{87}Rb (radioactive; $t_{1/2} = 4.7 \times 10^{10}$ years).

The radioactive decay of ^{87}Rb leads to ^{87}Sr .

In Greenland one finds a gneiss (= silicate mineral) containing both strontium and rubidium.

1.5 What is the equation rate law describing the formation of ^{87}Sr from ^{87}Rb as a function of time?

1.6 Assume that the isotope ratio $^{87}\text{Sr}/^{86}\text{Sr}$ (as determined by mass spectrometry) and the isotope ratio $^{87}\text{Rb} : ^{86}\text{Sr}$ are known for the gneiss. What is the mathematical relationship with which one can calculate the age of the gneiss?

Official English text of the problem.

Answers

- **1.1** Interpreting α as the decay constant λ ,

$$\alpha = \lambda = \frac{\ln 2}{t_{1/2}}.$$

- **1.2** The wood was approximately 1.03×10^3 years old in 1983. The tree was cut around **948 CE**.
- **1.3** The age uncertainty is approximately

$$\Delta t \approx \pm 1.4 \times 10^2 \text{ years.}$$

- **1.4** The isotope number ratio is

$$\frac{N(^{12}\text{C})}{N(^{14}\text{C})} \approx 8.39 \times 10^{11}.$$

- **1.5** Let $P(t)$ and $D(t)$ be the numbers of ^{87}Rb and ^{87}Sr atoms, respectively. Then

$$\frac{dD}{dt} = \lambda_{\text{Rb}} P_0 e^{-\lambda_{\text{Rb}} t}, \quad D(t) = D_0 + P_0 (1 - e^{-\lambda_{\text{Rb}} t}),$$

where $\lambda_{\text{Rb}} = \ln 2 / (4.7 \times 10^{10} \text{ yr})$.

- **1.6** Define the present isotope number ratios

$$R = \left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}} \right)_t, \quad Q = \left(\frac{^{87}\text{Rb}}{^{86}\text{Sr}} \right)_t.$$

For a closed system with initial strontium ratio R_0 ,

$$t = \frac{4.7 \times 10^{10} \text{ yr}}{\ln 2} \ln \left(1 + \frac{R - R_0}{Q} \right).$$

Taking the listed strontium composition as the initial composition gives $R_0 = 7.00/9.86 \approx 0.710$.

Solution

1.1

At one half-life, half the original radioactive atoms remain:

$$\frac{N(t_{1/2})}{N_0} = \frac{1}{2} = e^{-\lambda t_{1/2}}.$$

Taking natural logarithms gives

$$-\ln 2 = -\lambda t_{1/2},$$

and therefore

$$\lambda = \frac{\ln 2}{t_{1/2}}.$$

For carbon-14,

$$\lambda_C = \frac{\ln 2}{5730 \text{ yr}} = 1.20968 \times 10^{-4} \text{ yr}^{-1}.$$

1.2

The activity is proportional to the number of carbon-14 atoms:

$$A = \lambda_C N.$$

Consequently, the specific activity of the wood follows the same exponential law:

$$A(t) = A_0 e^{-\lambda_C t}.$$

Taking $A_0 = 13.6 \text{ min}^{-1} \text{ g}^{-1}$ at the time the tree was cut and $A = 12.0 \text{ min}^{-1} \text{ g}^{-1}$ in 1983,

$$t = \frac{1}{\lambda_C} \ln \frac{A_0}{A} = \frac{5730 \text{ yr}}{\ln 2} \ln \frac{13.6}{12.0} = 1034.68 \text{ yr}.$$

The corresponding calendar year is

$$1983 - 1034.68 = 948.32.$$

Thus, within the dating model specified in the problem, the tree was cut around

$$\boxed{948 \text{ CE.}}$$

1.3

Treating the initial activity and half-life as fixed, differentiate the age formula with respect to the measured activity:

$$t(A) = \frac{1}{\lambda_C} \ln \frac{A_0}{A}, \quad \frac{dt}{dA} = -\frac{1}{\lambda_C A}.$$

The magnitude of the first-order age uncertainty is therefore

$$\Delta t \approx \left| \frac{dt}{dA} \right| \Delta A = \frac{\Delta A}{\lambda_C A}.$$

Substitution gives

$$\Delta t = \frac{5730 \text{ yr}}{\ln 2} \frac{0.2 \text{ min}^{-1} \text{ g}^{-1}}{12.0 \text{ min}^{-1} \text{ g}^{-1}} = 137.78 \text{ yr}.$$

Hence

$$t \approx (1.03 \pm 0.14) \times 10^3 \text{ yr.}$$

The exact endpoint calculation gives

$$t(12.2) = 898.04 \text{ yr}, \quad t(11.8) = 1173.62 \text{ yr},$$

or $1034.68^{+138.94}_{-136.64}$ yr, consistent with the rounded uncertainty of approximately ± 140 years.

1.4

Consider 1.000 g of carbon participating in the natural cycle. Convert the carbon-14 decay constant to inverse minutes:

$$\lambda_C = \frac{\ln 2}{5730 \times 365 \times 24 \times 60 \text{ min}} = 2.30152 \times 10^{-10} \text{ min}^{-1}.$$

Since its activity is 13.6 min^{-1} , the number of carbon-14 atoms is

$$N(^{14}\text{C}) = \frac{A}{\lambda_C} = \frac{13.6 \text{ min}^{-1}}{2.30152 \times 10^{-10} \text{ min}^{-1}} = 5.90913 \times 10^{10}.$$

Neglecting the minute carbon-14 contribution and using the isotope mass numbers to approximate their molar masses, the mean carbon molar mass is

$$M_C = (0.9890 \times 12 + 0.0110 \times 13) \text{ g mol}^{-1} = 12.011 \text{ g mol}^{-1}.$$

Using the standard Avogadro constant, $N_A \approx 6.022 \times 10^{23} \text{ mol}^{-1}$,

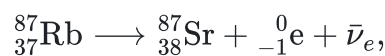
$$N(^{12}\text{C}) = 0.9890 \frac{1.000 \text{ g}}{12.011 \text{ g mol}^{-1}} N_A \approx 4.959 \times 10^{22}.$$

Thus the required atom-number ratio is

$$\frac{N(^{12}\text{C})}{N(^{14}\text{C})} = \frac{4.959 \times 10^{22}}{5.90913 \times 10^{10}} \approx 8.39 \times 10^{11}.$$

1.5

Rubidium-87 undergoes beta-minus decay to strontium-87:



where $\bar{\nu}_e$ is an electron antineutrino. The mass number remains 87, and charge is conserved because $37 = 38 - 1$.

Let $P(t)$ denote the number of rubidium-87 atoms and $D(t)$ the number of strontium-87 atoms. Each parent decay produces one stable daughter atom. In a closed system,

$$\frac{dP}{dt} = -\lambda_{\text{Rb}} P, \quad \frac{dD}{dt} = \lambda_{\text{Rb}} P, \quad \lambda_{\text{Rb}} = \frac{\ln 2}{4.7 \times 10^{10} \text{ yr}}.$$

Since $P(t) = P_0 e^{-\lambda_{\text{Rb}} t}$,

$$\frac{dD}{dt} = \lambda_{\text{Rb}} P_0 e^{-\lambda_{\text{Rb}} t}.$$

Integrating from time zero to time t gives

$$D(t) - D_0 = \int_0^t \lambda_{\text{Rb}} P_0 e^{-\lambda_{\text{Rb}} \tau} d\tau = P_0 (1 - e^{-\lambda_{\text{Rb}} t}).$$

Therefore,

$$D(t) = D_0 + P_0 (1 - e^{-\lambda_{\text{Rb}} t}).$$

Here D_0 includes the strontium-87 already present when the system formed.

1.6

The initial number of rubidium-87 atoms can be expressed using its present number:

$$P_0 = P(t) e^{\lambda_{\text{Rb}} t}.$$

Substituting this into the daughter-growth equation yields

$$D(t) = D_0 + P(t) (e^{\lambda_{\text{Rb}} t} - 1).$$

Strontium-86 is stable and is neither produced nor consumed by this decay. Its number, $S = N(^{86}\text{Sr})$, therefore remains constant in a closed system. Dividing by S gives

$$\frac{D(t)}{S} = \frac{D_0}{S} + \frac{P(t)}{S} (e^{\lambda_{\text{Rb}} t} - 1).$$

In terms of isotope ratios,

$$R = R_0 + Q (e^{\lambda_{\text{Rb}} t} - 1).$$

Rearranging,

$$e^{\lambda_{\text{Rb}} t} = 1 + \frac{R - R_0}{Q},$$

so

$$t = \frac{1}{\lambda_{\text{Rb}}} \ln \left(1 + \frac{R - R_0}{Q} \right).$$

Taking the supplied strontium isotope composition to represent the initial composition,

$$R_0 = \frac{7.00}{9.86} = 0.709939 \dots,$$

and the requested relationship becomes

$$t = \frac{4.7 \times 10^{10} \text{ yr}}{\ln 2} \ln \left[1 + \frac{(^{87}\text{Sr}/^{86}\text{Sr})_t - 7.00/9.86}{(^{87}\text{Rb}/^{86}\text{Sr})_t} \right].$$

This age represents the elapsed time since the mineral system became closed to rubidium and strontium exchange.

The solution was checked against the official solution.

Problem 2: Metal carbonyls and the eighteen-electron rule

Ludwig Mond discovered before the turn of this century that finely divided nickel reacts with carbon monoxide forming tetracarbonylnickel, $\text{Ni}(\text{CO})_4$, a colourless, very volatile liquid. The composition of $\text{Ni}(\text{CO})_4$ provides an example of the noble gas rule ("EAN rule").

Problems:

2.1 Use the eighteen-electron rule (noble gas rule) to predict the formula of the binary carbonyls of $\text{Fe}(0)$ and $\text{Cr}(0)$.

2.2 What composition would the eighteen-electron rule predict for the most simple binary chromium(0)-nitrosyl compound?

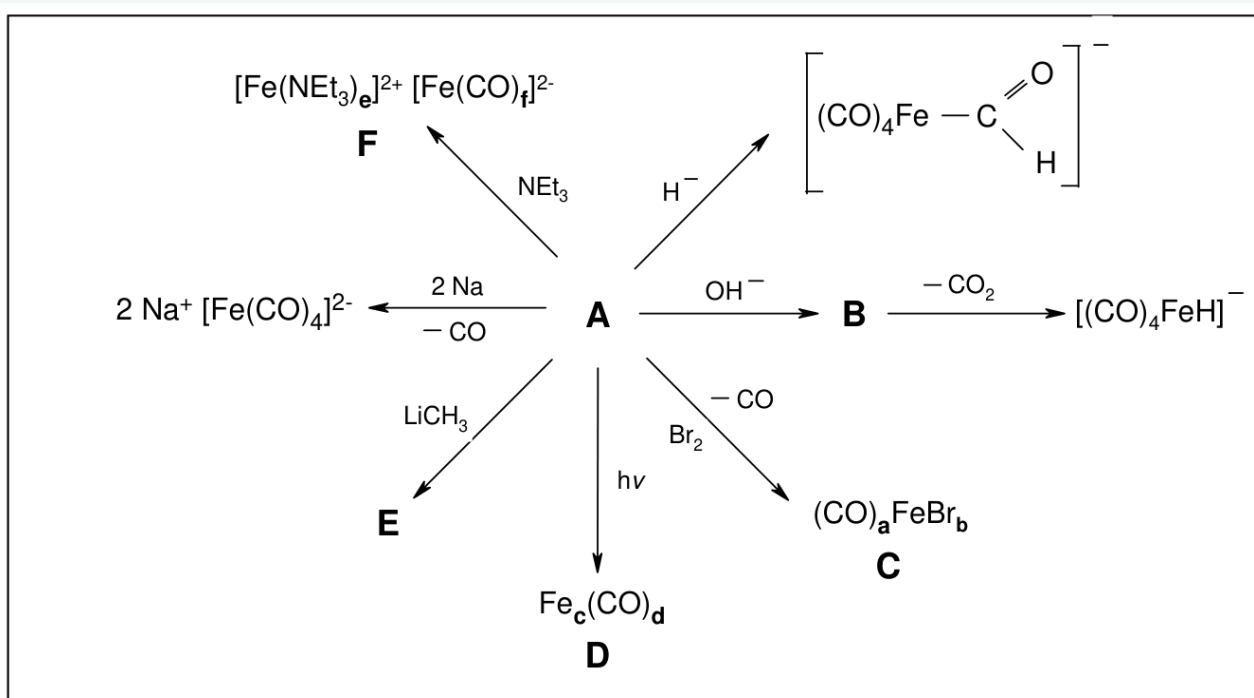
2.3 Explain why $\text{Mn}(0)$ and $\text{Co}(0)$ do not form so-called mononuclear carbonyl complexes of the type $\text{M}(\text{CO})_x$ (M = metal), but rather compounds with metal-metal bonding.

2.4 Suggest structures of $\text{Ni}(\text{CO})_4$, $\text{Mn}_2(\text{CO})_{10}$ and $\text{Co}_2(\text{CO})_8$.

2.5 State whether $\text{V}(\text{CO})_6$ and the compounds mentioned in a) and d) are diamagnetic or paramagnetic.

2.6 Why are the carbon monoxide ligands bound to metals much more strongly than to boron in borane adducts (e.g. $\text{R}_3\text{B}-\text{CO}$; R = alkyl)?

2.7 Determine the composition of the compounds labeled **A - F** in the following reaction scheme:



Hints:

a) **C** has the following analysis: C, 14.75 % ; Br, 48.90 % .

b) **D** contains 30.70 % Fe; the molecular mass is 363.8 a.m.u.

c) Excess triethylamine is used for the synthesis of **F**. **F** contains 5.782 % C and 10.11 % N.

2.8 Why is the compound **F** formed in the disproportionation reaction (given in g)), and not the compositional isomer $[\text{Fe}(\text{CO})_f]^{2+}[\text{Fe}(\text{NEt}_3)_e]^{2-}$?

2.9 The eighteen-electron rule is also satisfied by a compound prepared from elementary chromium and benzene.

i) Draw the formula of this complex.

ii) Which complex with the analogous structure is prepared by the reaction of iron powder with cyclopentadiene? Write the chemical equation for its formation.

Official English text of the problem.

Answers

Names, SMILES, and detailed structural descriptions are supplied in the corresponding solution parts.

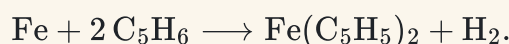
- **2.1:** Iron pentacarbonyl, $\text{Fe}(\text{CO})_5$, and chromium hexacarbonyl, $\text{Cr}(\text{CO})_6$.
- **2.2:** Tetranitrosylchromium, $\text{Cr}(\text{NO})_4$, counting each linear nitrosyl as a three-electron donor.
- **2.3:** Their odd metal-electron counts cannot reach 18 by adding two-electron carbonyl ligands. Metal-metal bonding supplies the additional electron counted at each metal.
- **2.4:** $\text{Ni}(\text{CO})_4$ is tetrahedral. $\text{Mn}_2(\text{CO})_{10}$ has an Mn-Mn bond and ten terminal carbonyls. The usual bridged structure of $\text{Co}_2(\text{CO})_8$ has a Co-Co bond, six terminal carbonyls, and two bridging carbonyls; an unbridged isomer also exists.
- **2.5:** $\text{V}(\text{CO})_6$ is paramagnetic, with one unpaired electron. $\text{Fe}(\text{CO})_5$, $\text{Cr}(\text{CO})_6$, $\text{Ni}(\text{CO})_4$, $\text{Mn}_2(\text{CO})_{10}$, and $\text{Co}_2(\text{CO})_8$ are diamagnetic.
- **2.6:** Metal-carbonyl bonding combines carbon-to-metal σ donation with metal-to-carbonyl π back-donation. Trialkylboranes cannot provide comparable back-donation.
- **2.7:**

Label	Composition
A	$\text{Fe}(\text{CO})_5$
B	$[\text{Fe}(\text{CO})_4(\text{COOH})]^-$, with an Fe-C bond to the hydroxycarbonyl group
C	$\text{Fe}(\text{CO})_4\text{Br}_2$: $a = 4$, $b = 2$
D	$\text{Fe}_2(\text{CO})_9$: $c = 2$, $d = 9$
E	$\text{Li}[\text{Fe}(\text{CO})_4(\text{COCH}_3)]$, the lithium salt of an acetyl complex
F	$[\text{Fe}(\text{NEt}_3)_6]^{2+}[\text{Fe}(\text{CO})_4]^{2-}$: $e = 6$, $f = 4$

The identification of **F** requires recognizing that its printed carbon percentage is inconsistent; the calculated value is **57.82%**, not 5.782%.

- **2.8:** **F** places π -accepting carbonyls on electron-rich iron(–II) and amine donors on iron(II). Both ions have 18 electrons; reversing the ligand allocation gives 14- and 22-electron ions.
- **2.9(i):** Bis(benzene)chromium, $\text{Cr}(\text{C}_6\text{H}_6)_2$, an η^6, η^6 sandwich complex.

- **2.9(ii):** Ferrocene, $\text{Fe}(\text{C}_5\text{H}_5)_2$, an η^5, η^5 sandwich complex:



Solution

Coordination SMILES below use $\rightarrow$ and $\leftarrow$ for dative bonds. Formal charges in a SMILES are not, by themselves, metal oxidation states. Bridging carbonyls are represented by carbon atoms bonded to both metals, with a double bond to oxygen. For sandwich complexes, component SMILES are accompanied by explicit descriptions of the haptic bonding, which ordinary SMILES cannot adequately express.

For numerical checks, conventional atomic molar masses are used: C, 12.011; H, 1.008; N, 14.007; O, 15.999; Fe, 55.845; and Br, 79.904, all in g mol^{-1} .

2.1

In neutral-atom electron counting, a metal contributes its group number and each terminal carbon monoxide ligand contributes two electrons. Carbon monoxide, CO, has SMILES $[\text{C-}]\#[\text{O+}]$ and coordinates through carbon.

For iron:

$$8 + 2n = 18 \implies n = 5.$$

Thus the compound is **iron pentacarbonyl**, $\text{Fe}(\text{CO})_5$, SMILES $[\text{Fe}](\leftarrow[\text{C-}]\#[\text{O+}])(\leftarrow[\text{C-}]\#[\text{O+}])(\leftarrow[\text{C-}]\#[\text{O+}])(\leftarrow[\text{C-}]\#[\text{O+}])(\leftarrow[\text{C-}]\#[\text{O+}])$.

Its usual coordination geometry is trigonal bipyramidal.

For chromium:

$$6 + 2n = 18 \implies n = 6.$$

Thus the compound is **chromium hexacarbonyl**, $\text{Cr}(\text{CO})_6$, SMILES $[\text{Cr}](\leftarrow[\text{C-}]\#[\text{O+}])(\leftarrow[\text{C-}]\#[\text{O+}])(\leftarrow[\text{C-}]\#[\text{O+}])(\leftarrow[\text{C-}]\#[\text{O+}])(\leftarrow[\text{C-}]\#[\text{O+}])(\leftarrow[\text{C-}]\#[\text{O+}])$.

Its coordination geometry is octahedral.

2.2

Nitrogen monoxide, or nitric oxide, NO, SMILES $[\text{N}]=\text{O}$, is an odd-electron molecule. A linear, N-bound nitrosyl ligand contributes **three electrons** in neutral-fragment counting.

Consequently,

$$6 + 3n = 18 \implies n = 4.$$

The predicted compound is **tetranitrosylchromium**, $\text{Cr}(\text{NO})_4$, connectivity SMILES $\text{O}=\text{N}[\text{Cr}](\text{N}=\text{O})(\text{N}=\text{O})\text{N}=\text{O}$.

The electron count assumes linear Cr–N–O units; their bond angles are not encoded by this SMILES.

2.3

Manganese and cobalt contribute seven and nine electrons, respectively. For neutral mononuclear carbonyls, the required numbers of ligands would be

$$\begin{array}{lll} \text{Mn:} & 7 + 2n = 18 & \implies n = 5.5, \\ \text{Co:} & 9 + 2n = 18 & \implies n = 4.5. \end{array}$$

Neither is an integer. Adding two-electron donors to an odd metal-electron count always leaves an odd total.

A metal-metal single bond contributes one electron to the count at **each** metal. Thus the dimers can satisfy

$$\begin{array}{ll} \text{Mn}_2(\text{CO})_{10}: & 7 + 5(2) + 1 = 18 \quad \text{at each Mn,} \\ \text{unbridged Co}_2(\text{CO})_8: & 9 + 4(2) + 1 = 18 \quad \text{at each Co.} \end{array}$$

2.4

- **Tetracarbonylnickel**, $\text{Ni}(\text{CO})_4$, SMILES [Ni](<-[C-]#[O+])(<-[C-]#[O+])(<-[C-]#[O+])(<-[C-]#[O+])<-[C-]#[O+].

Place nickel at the centre of a tetrahedron and four carbon-bound carbonyl ligands at its vertices. The Ni-C-O units are approximately linear. Its electron count is $10 + 4(2) = 18$.

- **Dimanganese decacarbonyl**, $\text{Mn}_2(\text{CO})_{10}$, SMILES [Mn](<-[C-]#[O+])(<-[C-]#[O+])(<-[C-]#[O+])(<-[C-]#[O+])<-[C-]#[O+][Mn](<-[C-]#[O+])(<-[C-]#[O+])(<-[C-]#[O+])(<-[C-]#[O+])<-[C-]#[O+].

Draw an Mn-Mn single bond, with five terminal carbonyl ligands on each manganese. Counting the other manganese as a coordination partner, each metal has approximately octahedral coordination: four equatorial carbonyls and one axial carbonyl opposite the Mn-Mn bond. The two equatorial sets are staggered, approximately 45° apart when viewed along that bond. There are no bridging carbonyls.

- **Dicobalt octacarbonyl, bridged form**, $\text{Co}_2(\text{CO})_8$, SMILES [Co]12(<-[C-]#[O+])(<-[C-]#[O+])(<-[C-]#[O+])(<-[C-]#[O+])<-[C-]#[O+][Co](<-[C-]#[O+])(<-[C-]#[O+])(<-[C-]#[O+])(<-[C-]#[O+])<-[C-]#[O+].

Draw a Co-Co bond, three terminal carbonyls on each cobalt, and two carbonyl groups whose carbon atoms each bridge both cobalt atoms. Each bridging carbonyl contributes one electron to each metal in neutral counting:

$$9 + 3(2) + 2(1) + 1 = 18.$$

An **unbridged isomer of dicobalt octacarbonyl** also occurs, particularly in solution. Its SMILES is [Co](<-[C-]#[O+])(<-[C-]#[O+])(<-[C-]#[O+])(<-[C-]#[O+])<-[C-]#[O+][Co](<-[C-]#[O+])(<-[C-]#[O+])(<-[C-]#[O+])(<-[C-]#[O+])<-[C-]#[O+].

It has four terminal carbonyls per cobalt and a Co-Co bond. Counting the other cobalt, each metal has approximately trigonal-bipyramidal coordination. Both arrangements satisfy the eighteen-electron rule.

2.5

The references to a) and d) are interpreted as **2.1** and **2.4**.

Vanadium hexacarbonyl, $\text{V}(\text{CO})_6$, has SMILES [V](<-[C-]#[O+])(<-[C-]#[O+])(<-[C-]#[O+])(<-[C-]#[O+])(<-[C-]#[O+])(<-[C-]#[O+])<-[C-]#[O+].

Its electron count is

$$5 + 6(2) = 17.$$

It has one unpaired electron and is therefore paramagnetic.

Compound	Electron count per metal	Magnetic behaviour
$\text{V}(\text{CO})_6$	17	Paramagnetic; one unpaired electron
$\text{Fe}(\text{CO})_5$	18	Diamagnetic
$\text{Cr}(\text{CO})_6$	18	Diamagnetic
$\text{Ni}(\text{CO})_4$	18	Diamagnetic
$\text{Mn}_2(\text{CO})_{10}$	18, including the Mn–Mn bond	Diamagnetic
$\text{Co}_2(\text{CO})_8$	18, including the Co–Co bond and any bridges	Diamagnetic

The latter carbonyls have paired-electron ground states; in the dimers, the metal–metal bond pairs the electrons associated with the otherwise odd-electron fragments.

2.6

Metal–carbonyl bonding has two mutually reinforcing components:

1. **σ donation:** the carbon-centred lone pair of the carbonyl ligand donates into a suitable vacant metal orbital.
2. **π back-donation:** occupied metal orbitals donate electron density into the carbonyl ligand's vacant antibonding π^* orbitals.

Back-donation strengthens the metal–carbon bond while weakening the carbon–oxygen bond.

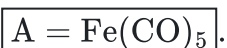
A **trialkylborane–carbon monoxide adduct**, $\text{R}_3\text{B}-\text{CO}$, can be represented generically by SMILES `*[B-](*)C#[O+]`, where each `*` denotes an alkyl group.

The electron-deficient boron atom accepts σ donation, but it lacks the suitable occupied orbitals needed for comparable back-donation. The additional stabilization present in transition-metal carbonyls is therefore largely absent.

2.7

A — iron pentacarbonyl

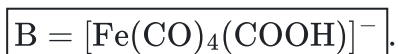
The hydride-addition branch retains four unchanged carbonyl ligands and converts one carbonyl into a formyl ligand. The sodium branch likewise produces a tetracarbonyl anion while releasing one carbon monoxide molecule. Both identify



Its name and SMILES are given in 2.1.

B — tetracarbonyl(hydroxycarbonyl)ferrate(0)

Hydroxide attacks the carbon atom of a coordinated carbonyl, producing a hydroxycarbonyl ligand:



Its SMILES is `OC(=O)[Fe-](C=[O+])(C=[O+])(C=[O+])C=[O+]`.

The connectivity is $\text{Fe}-\text{C}(=\text{O})-\text{OH}$, rather than an oxygen-bound formate group. Loss of carbon dioxide, accompanied by transfer of hydrogen to iron, gives the hydride shown in the scheme.

C — dibromidotetracarbonyliron(II)

For $\text{Fe}(\text{CO})_a\text{Br}_b$, the analytical carbon-to-bromine atomic ratio is

$$\frac{a}{b} = \frac{14.75/12.011}{48.90/79.904} = 2.007 \approx 2.$$

Thus $a \approx 2b$. Since carbonyl is neutral and each bromido ligand has charge -1 , iron has oxidation state $+b$. The eighteen-electron condition is

$$(8 - b) + 2a + 2b = 18,$$

or

$$2a + b = 10.$$

Together these give

$$\boxed{a = 4, \quad b = 2, \quad \text{C} = \text{Fe}(\text{CO})_4\text{Br}_2}.$$

Its SMILES is [Fe](Br)(Br)(<-[C-]#[O+])(<-[C-]#[O+])(<-[C-]#[O+])<-[C-]#[O+].

The coordination is octahedral; the stated composition data do not establish a cis/trans arrangement.

The calculated molar mass and percentages are

$$M = 55.845 + 4(28.010) + 2(79.904) = 327.693 \text{ g mol}^{-1},$$
$$w_{\text{C}} = 14.66\%, \quad w_{\text{Br}} = 48.77\%.$$

These differ slightly from the printed values, although the analytical ratio and electron count support the formula above.

D — diiron nonacarbonyl

The given molecular mass corresponds to a molar mass of 363.8 g mol^{-1} . The number of iron atoms is

$$c = \frac{0.3070(363.8 \text{ g mol}^{-1})}{55.845 \text{ g mol}^{-1}} = 1.99994 \approx 2.$$

The remaining mass determines the number of carbonyls:

$$d = \frac{363.8 - 2(55.845)}{28.010} = 9.0007 \approx 9.$$

Therefore

$$\boxed{\text{D} = \text{Fe}_2(\text{CO})_9}.$$

A SMILES for the usual structure is [Fe]123(<-[C-]#[O+])(<-[C-]#[O+])(<-[C-]#[O+])[Fe](<-[C-]#[O+])(<-[C-]#[O+])(<-[C-]#[O+])(C1=O)(C2=O)C3=O.

This structure has an Fe–Fe bond, six terminal carbonyls, and three bridging carbonyls. Each iron has

$$8 + 3(2) + 3(1) + 1 = 18$$

electrons.

E — lithium acetyl(tetracarbonyl)ferrate(0)

The methyl nucleophile attacks a coordinated carbonyl carbon, just as hydride gives the formyl complex. It produces an acetyl ligand:

$$\boxed{\text{E} = \text{Li}[\text{Fe}(\text{CO})_4(\text{COCH}_3)]}.$$

Its SMILES is [Li+].CC(=O)[Fe-](<-[C-]#[O+])(<-[C-]#[O+])(<-[C-]#[O+])<-[C-]#[O+].

The acetyl group is attached through its carbonyl carbon: Fe-C(=O)-CH3.

F — hexakis(triethylamine)iron(II) tetracarbonylferrate(−II)

For the carbonyl anion, the electron count is

$$8 + 2 + 2f = 18,$$

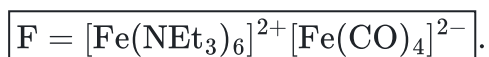
giving $f = 4$.

For the iron(II) amine cation,

$$8 - 2 + 2e = 18,$$

giving $e = 6$.

Thus the expected salt is



Its SMILES is [Fe+2](<-N(CC)(CC)CC)(<-N(CC)(CC)CC)(<-N(CC)(CC)CC)(<-N(CC)(CC)CC)(<-N(CC)(CC)CC)(<-N(CC)(CC)CC)<-N(CC)(CC)CC.[Fe-2](<-[C-]#[O+])(<-[C-]#[O+])(<-[C-]#[O+])<-[C-]#[O+].

The ions are **hexakis(triethylamine)iron(II)** and **tetracarbonylferrate(−II)**. Their expected coordination geometries are octahedral and tetrahedral, respectively.

The nitrogen analysis independently checks e . Triethylamine has molar mass

$$M(\text{NEt}_3) = 101.193 \text{ g mol}^{-1}.$$

With $f = 4$,

$$M_F = 223.730 + 101.193e \text{ g mol}^{-1},$$

so

$$\frac{14.007e}{223.730 + 101.193e} = 0.1011 \implies e = 5.9896 \approx 6.$$

For the resulting formula,

$$\begin{aligned} M_F &= 830.888 \text{ g mol}^{-1}, \\ w_C &= \frac{40(12.011)}{830.888} \times 100 = 57.82\%, \\ w_N &= \frac{6(14.007)}{830.888} \times 100 = 10.11\%. \end{aligned}$$

The printed **5.782% carbon is impossible** for the stated ligand composition. Every triethylamine nitrogen already requires six carbon atoms, whereas the printed percentages imply

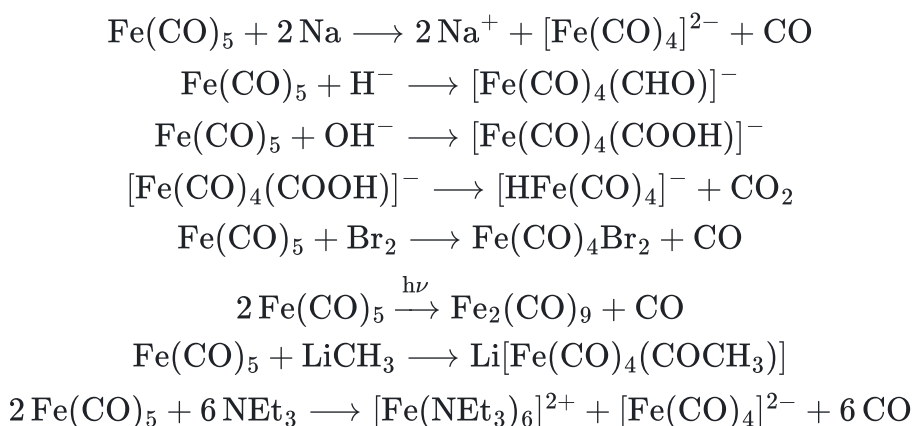
$$\frac{n_C}{n_N} = \frac{5.782/12.011}{10.11/14.007} \approx 0.667 < 6.$$

Additional carbonyl ligands would only increase this ratio. The intended carbon percentage is evidently **57.82%**.

The other species needed to describe the reaction scheme are:

Species	Name	SMILES
NEt ₃	Triethylamine	CCN(CC)CC
LiCH ₃	Methyl lithium, ionic representation	[Li+].[CH3-]
Br ₂	Bromine	BrBr
OH ⁻	Hydroxide ion	[OH-]
H ⁻	Hydride ion	[H-]
Na ⁺	Sodium ion	[Na+]
CO ₂	Carbon dioxide	O=C=O
[Fe(CO) ₄ (CHO)] ⁻	Tetracarbonyl(formyl)ferrate(0)	O=C[Fe-](<-[C-]#[O+])(<-[C-]#[O+])(<-[C-]#[O+])<-[C-]#[O+]
[HFe(CO) ₄] ⁻	Tetracarbonylhydridoferrate(0)	[H][Fe-](<-[C-]#[O+])(<-[C-]#[O+])(<-[C-]#[O+])<-[C-]#[O+]

The complete balanced reactions are:



All conserve both atoms and charge.

2.8

The disproportionation converts two iron(0) centres into iron(II) and iron(-II).

Carbon monoxide is a strong π -acceptor ligand. It stabilizes electron-rich iron(-II) through substantial back-donation into its π^* orbitals. Triethylamine is predominantly a σ -donor and preferentially stabilizes the electron-poor iron(II) centre.

The observed ligand allocation also gives 18 electrons to both ions:

$$\begin{aligned}
 [\text{Fe}(\text{NEt}_3)_6]^{2+} &: 8 - 2 + 6(2) = 18, \\
 [\text{Fe}(\text{CO})_4]^{2-} &: 8 + 2 + 4(2) = 18.
 \end{aligned}$$

The proposed reversal would instead give:

- Hypothetical **tetracarbonyliron(II) cation**, $[\text{Fe}(\text{CO})_4]^{2+}$, SMILES `[Fe+2](<-[C-]#[O+])(<-[C-]#[O+])(<-[C-]#[O+])<-[C-]#[O+]`:

$$8 - 2 + 4(2) = 14.$$

- Hypothetical **hexakis(triethylamine)ferrate(-II) anion**, $[\text{Fe}(\text{NEt}_3)_6]^{2-}$, SMILES [Fe-2](<-N(CC)(CC)CC)(<-N(CC)(CC)CC)(<-N(CC)(CC)CC)(<-N(CC)(CC)CC)(<-N(CC)(CC)CC)(<-N(CC)(CC)CC):

$$8 + 2 + 6(2) = 22.$$

Thus both ligand electronic preferences and electron counting favour **F**.

2.9(i)

Benzene, C_6H_6 , SMILES c1ccccc1, contributes six electrons when coordinated through all six ring carbon atoms.

Chromium contributes six electrons, so two benzene ligands give

$$6 + 2(6) = 18.$$

The complex is **bis(η^6 -benzene)chromium(0)**, $\text{Cr}(\text{C}_6\text{H}_6)_2$, component SMILES [Cr].c1ccccc1.c1ccccc1.

To draw it, place chromium midway between two parallel, planar benzene rings, with the metal and both ring centres on one perpendicular axis. Each ring binds through its entire six-carbon π system. The component SMILES does not encode these η^6 interactions.

The formal formation equation is



2.9(ii)

Cyclopenta-1,3-diene, C_5H_6 , has SMILES c1C=CC=C1. Its deprotonated ligand is the **cyclopentadienyl anion**, C_5H_5^- , SMILES [CH-]1CCCC1, a six- π -electron donor.

The analogous sandwich complex is **ferrocene**, or **bis(η^5 -cyclopentadienyl)iron(II)**:



Its component SMILES is [Fe+2].[CH-]1CCCC1.[CH-]1CCCC1.

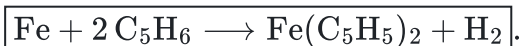
Draw iron between two parallel, planar five-membered rings, with the metal on the line joining their centres. Each ring coordinates through all five carbon atoms. The question does not require a particular relative rotational orientation of the rings.

With two anionic ligands, iron is formally iron(II), giving

$$(8 - 2) + 2(6) = 18$$

electrons.

The balanced formation equation is



The gaseous coproduct is **molecular hydrogen**, H_2 , SMILES [H][H].

The solution was checked against the official solution.

Problem 3: Spectrophotometric determination of the pK_a of a coloured weak acid

A weak acid of total concentration 2×10^{-2} M is dissolved in a buffer of pH = 8.8. The anion A^- of this acid is coloured and has a molar decadic absorption coefficient ε of $2.1 \times 10^4 \text{ cm}^2 \text{ mol}^{-1}$. A layer l of the solution with 1.0 cm thickness absorbs 60 percent of the incident luminous intensity I_o .

3.1 What is the equation relating the extinction to the thickness of the absorbing layer?

3.2 How large is the concentration of the acid anion in the buffer solution?

3.3 How large is the pK_a of the acid?

Official English text of the problem.

Answers

- **3.1** $E = \log_{10} \left(\frac{I_o}{I} \right) = \varepsilon cl$, with $c = [A^-]$ in mol cm^{-3} when using the stated units of ε .
- **3.2** $[A^-] \approx 1.9 \times 10^{-2} \text{ mol L}^{-1}$.
- **3.3** $\text{p}K_a \approx 7.5$ (calculated value 7.54).

Solution

3.1

The Beer–Lambert law relates the extinction (absorbance), E , to the absorbing species' concentration c and the optical path length l :

$$E = \log_{10} \left(\frac{I_o}{I} \right) = \varepsilon cl.$$

Equivalently,

$$I = I_o 10^{-\varepsilon cl}.$$

Here I_o and I are the incident and transmitted luminous intensities. With ε in $\text{cm}^2 \text{ mol}^{-1}$ and l in cm, concentration must be expressed in mol cm^{-3} , making E dimensionless.

3.2

Since 60 percent of the incident intensity is absorbed, 40 percent is transmitted:

$$\frac{I}{I_o} = 0.40, \quad E = -\log_{10}(0.40) = 0.397940.$$

Therefore,

$$[A^-] = \frac{E}{\varepsilon l} = \frac{0.397940}{(2.1 \times 10^4 \text{ cm}^2 \text{ mol}^{-1})(1.0 \text{ cm})} = 1.89495 \times 10^{-5} \text{ mol cm}^{-3}.$$

Using $1 \text{ L} = 10^3 \text{ cm}^3$,

$$[\text{A}^-] = 1.89495 \times 10^{-2} \text{ mol L}^{-1} \approx 1.9 \times 10^{-2} \text{ M}.$$

3.3

Denote the undissociated weak acid by HA and its conjugate base by A^- . Their molecular structures are unspecified, so specific chemical names and SMILES cannot be assigned.

The acid dissociation equilibrium is



where H^+ is the hydrogen ion, $[\text{H}^+]$. In the concentration approximation,

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}.$$

The analytical concentration gives the mass balance

$$[\text{HA}] + [\text{A}^-] = 2.0 \times 10^{-2} \text{ M}.$$

Retaining extra digits during the subtraction,

$$[\text{HA}] = 0.0200000 - 0.0189495 = 1.05048 \times 10^{-3} \text{ M}.$$

Taking logarithms of the equilibrium expression gives

$$\text{pH} = \text{p}K_a + \log_{10} \left(\frac{[\text{A}^-]}{[\text{HA}]} \right).$$

Thus,

$$\begin{aligned} \text{p}K_a &= 8.8 - \log_{10} \left(\frac{1.89495 \times 10^{-2}}{1.05048 \times 10^{-3}} \right) \\ &= 8.8 - \log_{10}(18.039) \\ &= 7.5438. \end{aligned}$$

Hence, to a precision consistent with the supplied data,

$$\boxed{\text{p}K_a \approx 7.5}.$$

The solution was checked against the official solution.

Problem 4: Formula of a gaseous hydrocarbon from its combustion

15 cm³ of a gaseous hydrocarbon C_xH_y are mixed with 120 cm³ oxygen and ignited. After the reaction the burned gases are shaken with concentrated aqueous KOH solution. A part of the gases is completely absorbed while 67.5 cm³ gases remain. It has the same temperature and pressure as the original unburned mixture.

4.1 What is the composition of the remaining gas? Explain.

4.2 How large is the change in the amount of substance per mole of a hydrocarbon C_xH_y when this is burned completely?

4.3 What is the chemical formula of the hydrocarbon used for the experiment?

Give the steps of the calculation.

Answers

- **4.1:** The remaining gas is oxygen, O_2 , SMILES $O=O$, with volume 67.5 cm^3 , neglecting residual water vapour.
- **4.2:** Counting all combustion products, the change is $\left(\frac{y}{4} - 1\right)$ mol per mole of hydrocarbon. After removal of water and carbon dioxide, the measured gas amount decreases by $\left(1 + x + \frac{y}{4}\right)$ mol per mole of hydrocarbon.
- **4.3:** The intended hydrocarbon is **ethane**, C_2H_6 , SMILES CC , under the usual assumption of an ordinary stable gaseous hydrocarbon.

Solution

4.1

Complete combustion produces carbon dioxide, CO_2 , SMILES $O=C=O$, and water, H_2O , SMILES O :



Water is treated as removed from the measured gas by cooling and contact with the concentrated aqueous solution. Carbon dioxide is absorbed by potassium hydroxide, KOH , SMILES $[K+] \cdot [OH-]$:



The salt formed is potassium carbonate, K_2CO_3 , represented by the ionic SMILES $[K+] \cdot [K+] \cdot [O-]C(=O)[O-]$.

Under this complete-combustion model, the remaining gas must therefore be excess oxygen or unreacted hydrocarbon. If oxygen had been exhausted, the volume of unreacted hydrocarbon could not exceed its initial volume, 15 cm^3 , at the same temperature and pressure. Since

$$67.5 \text{ cm}^3 > 15 \text{ cm}^3,$$

oxygen was in excess. The hydrocarbon burned completely, leaving **oxygen** after the products were removed.

4.2

For one mole of hydrocarbon, the balanced combustion equation gives

$$n_{\text{reactants}} = \left(1 + x + \frac{y}{4}\right) \text{ mol},$$

and, counting both carbon dioxide and water,

$$n_{\text{products}} = \left(x + \frac{y}{2}\right) \text{ mol}.$$

Hence the change, defined as products minus reactants, is

$$\Delta n_{\text{total}} = \left(\frac{y}{4} - 1\right) \text{ mol per mole of hydrocarbon.}$$

For interpreting the gas-volume experiment, the stages must be distinguished:

Stage	Change in gas amount per mole of hydrocarbon
Combustion, with all water remaining gaseous	$\left(\frac{y}{4} - 1\right) \text{ mol}$
After removal of water, before carbon dioxide absorption	$-\left(1 + \frac{y}{4}\right) \text{ mol}$
After removal of both water and carbon dioxide	$-\left(1 + x + \frac{y}{4}\right) \text{ mol}$

The last expression applies to the measured initial and final gas volumes.

4.3

At equal temperature and pressure, gas volumes are proportional to amounts of substance. The oxygen consumed is

$$V_{\text{O}_2, \text{ consumed}} = 120 - 67.5 = 52.5 \text{ cm}^3.$$

Thus each mole of hydrocarbon consumes

$$\frac{n_{\text{O}_2, \text{ consumed}}}{n_{\text{hydrocarbon}}} = \frac{52.5 \text{ cm}^3}{15 \text{ cm}^3} = 3.5$$

moles of oxygen. From the combustion equation,

$$x + \frac{y}{4} = 3.5,$$

so

$$\boxed{4x + y = 14}.$$

Equivalently, using the gas contraction after product removal,

$$1 + x + \frac{y}{4} = \frac{(15 + 120) - 67.5}{15} = 4.5.$$

For an ordinary neutral hydrocarbon, x, y are positive integers and the maximum hydrogen count is $y = 2x + 2$. Combining this bound with $y = 14 - 4x$ gives

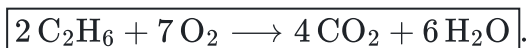
$$14 - 4x \leq 2x + 2 \implies x \geq 2,$$

while $y > 0$ requires $x \leq 3$. The formal possibilities are therefore

$$(x, y) = (2, 6) \quad \text{or} \quad (3, 2).$$

Of these, C_2H_6 is the ordinary stable gaseous hydrocarbon: **ethane**, SMILES `CC`. The formal alternative C_3H_2 requires unusual reactive or highly strained species, outside the intended scope of this elementary analysis.

Ethane burns according to



The volume check is

$$V_{\text{O}_2, \text{ consumed}} = \frac{7}{2}(15 \text{ cm}^3) = 52.5 \text{ cm}^3,$$

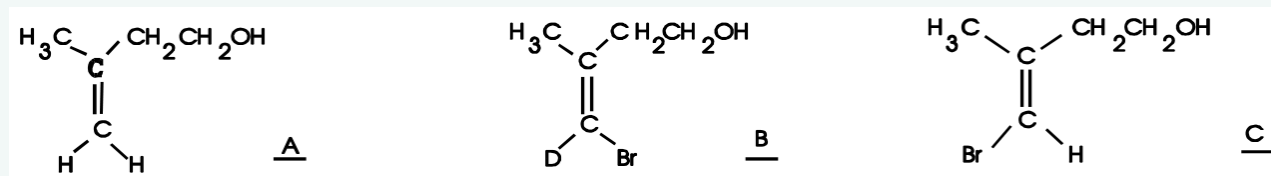
$$V_{\text{O}_2, \text{ remaining}} = 120 - 52.5 = \boxed{67.5 \text{ cm}^3},$$

exactly reproducing the measurement.

The solution was checked against the official solution.

Problem 5: Stereochemistry of the bromination-dehydrobromination of a monodeuterated alkene

One of the diastereotopic methylene protons at the double bond of **A** was selectively substituted by deuterium. Bromination and subsequent dehydrobromination yields the



deuteriated product **B** and the non-deuteriated product **C**.

5.1 Which configuration follows for the monodeuteriated **A** from the given reaction products?

5.2 The solution of this question requires the formulation of the reaction and a short argumentation why only **B** and **C** are formed.

Official English text of the problem.

Answers

- 5.1** Monodeuteriated **A** is **(3Z)-4-deuterio-3-methylbut-3-en-1-ol**, OCC/C(C)=C\[2H]. In the orientation shown, **D replaces the lower-right hydrogen**: D and the hydroxyethyl group lie on the same side of the double bond.
- 5.2** Anti bromination gives a racemic vicinal dibromide. Subsequent anti elimination gives:
- By loss of HBr: **B**, **(3Z)-4-bromo-4-deuterio-3-methylbut-3-en-1-ol**, OCC/C(C)=C(\Br)[2H].
- By loss of DBr: **C**, **(3E)-4-bromo-3-methylbut-3-en-1-ol**, OCC/C(C)=C/Br.

Solution

5.1 Configuration of monodeuteriated A

The unlabelled starting material is **3-methylbut-3-en-1-ol**, CCCC(C)=C. Number its chain from the alcohol end, so the double bond is between C₃ and C₄.

The stereochemical sequence established in part **5.2** requires the following arrangement in the labelled starting material:

Position in the supplied drawing	Substituent
Upper left, on C ₃	CH ₃
Upper right, on C ₃	CH ₂ CH ₂ OH
Lower left, on C ₄	H
Lower right, on C ₄	D

For the *E/Z* assignment:

- At C₃, CH₂CH₂OH has higher priority than CH₃: after the initial carbon tie, the attached-atom lists are (C, H, H) and (H, H, H).
- At C₄, D has higher priority than H, because the heavier isotope takes precedence.

The higher-priority groups are on the same side, so monodeuteriated **A** has the *Z* configuration.

5.2 Reaction sequence and stereochemical explanation

Bromination is **anti addition**, whereas the subsequent E2 elimination requires the departing bromine and the removed hydrogen isotope to be **antiperiplanar**.

Bromine, BrBr, adds according to the balanced equation

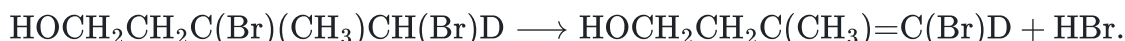


Addition from either face gives racemic **3,4-dibromo-4-deuterio-3-methylbutan-1-ol**, consisting of:

Enantiomer	Stereochemical SMILES
(3 <i>R</i> , 4 <i>R</i>)	<chem>OCC[C@](C)(Br)[C@H](Br)[2H]</chem>
(3 <i>S</i> , 4 <i>S</i>)	<chem>OCC[C@](C)(Br)[C@@H](Br)[2H]</chem>

The bromine attached to C₃ is eliminated together with either H or D from C₄. The following equations explicitly display the eliminated acid for atom balance; under basic conditions, the base captures that acid.

Loss of **hydrogen bromide**, HBr, gives **B**:



Loss of **deuterium bromide**, [2H]Br, gives **C**:



To follow the stereochemistry precisely, use a **Newman projection looking from C₃ toward C₄**. For one enantiomer, an accessible conformation has:

Carbon	Substituents at clock-face positions
Front, C ₃	Br at 12 o'clock; methyl at 8; hydroxyethyl at 4
Rear, C ₄	Br at 6 o'clock; H at 10; D at 2

These positions describe a conformation; the SMILES above encode configuration, not a particular conformation.

Eliminating H: Rotate the rear group until H is at 6 o'clock, anti to the front bromine. The rear D then lies at 10 o'clock and the rear Br at 2. Elimination therefore gives, in the paper's orientation, **D on the lower left and Br on the lower right**: exactly **B**. Its higher-priority groups, hydroxyethyl and Br, are on the same side, so **B is Z**.

Eliminating D: Instead, rotate the rear group until D is at 6 o'clock. The rear Br then lies at 10 o'clock and H at 2. Elimination gives **Br on the lower left and H on the lower right**: exactly **C**. Hydroxyethyl and Br are on opposite sides, so **C is E**.

In each elimination, the base removes the antiperiplanar H or D; the corresponding bond electrons form the new C₃=C₄ π bond while the C₃–Br bond breaks, releasing **bromide ion**, [Br[–]].

For elimination restoring the original double bond, there are two choices—remove H or remove D—and each fixes one product geometry. The mirror-image dibromide gives the same two achiral alkene products. Thus the sequence accounts for **B** and **C**. Putting D on the opposite side in the starting alkene would reverse both predicted product geometries, contradicting the supplied drawings.

The solution was checked against the official solution.

Problem 6: A C₅ hydrocarbon from pyrolysis fractions: dimerization, epoxidation and stereoisomers

A technically interesting C₅ hydrocarbon **A** is separated via dimerization from the for-runnings of the benzene-pyrolysis fraction. This is achieved either by heating to 140–150 °C under pressure or by heating over several hours at 100 °C. Then it is distilled out at 200 °C. Treatment of **A** with peroxyacetic acid under neutral conditions (sodium acetate and sodium carbonate) in dichloromethane at 20 °C yields a product **B**. **B** yields two isomeric products **C** and **D** (summary formula C₅H₈O₂) by the reaction with aqueous sodium carbonate solution. The main product **C** contains three different bound carbon atoms whereas in the minor product **D** five different carbon atoms are present. **C** is chiral.

6.1 Write the formulas of **A**, **B**, **C**, and **D** considering the stereochemical representation.

6.2 What is the name of the chemical reaction which is used for the above mentioned separation procedure?

6.3 Which stereochemical rules hold for the dimerization reaction?

6.4 Give the structure of the dimerization product.

6.5 Give the mechanism of the formation of **C** and **D** from **B**.

6.6 Which kind of isomers are **C** and **D**?

6.7 How many stereoisomers of **C** and **D** are principally (regardless of their synthetic availability) possible? Give their mutual stereochemical relations. Write their structural formulas.

Official English text of the problem.

Answers

- 6.1**
- A:** Cyclopenta-1,3-diene, C₅H₆: C1=CC=CC1.
- B:** Cyclopentadiene monoepoxide, **6-oxabicyclo[3.1.0]hex-2-ene**, C₅H₆O, as the racemic pair C1=CC[C@H]2O[C@@H]12 and C1=CC[C@@H]2O[C@H]12.
- C: trans-Cyclopent-4-ene-1,3-diol**, C₅H₈O₂, as the racemic pair O[C@@H]1C[C@H](O)C=C1 and O[C@H]1C[C@H](O)C=C1.
- D: trans-Cyclopent-3-ene-1,2-diol**, C₅H₈O₂, as the racemic pair O[C@H]1[C@H](O)C=CC1 and O[C@@H]1[C@@H](O)C=CC1.

- **6.2** A **Diels–Alder** $[4 + 2]$ **cycloaddition**, followed by a **retro-Diels–Alder reaction** when the monomer is recovered.
- **6.3** Suprafacial addition on both components, retention of the dienophile's relative stereochemistry, an **s-cis diene**, and preferential formation of the **endo** adduct.
- **6.4** The usual major dimer is racemic **endo-dicyclopentadiene**, $C_{10}H_{12}$:
 $C1=C[C@@H]2[C@H]3C=CC[C@H]3[C@H]1C2$ and its enantiomer
 $C1=C[C@H]2[C@@H]3C=CC[C@@H]3[C@@H]1C2$.
- **6.5** **C** forms by anti allylic S_N2' opening, with migration of the double bond; **D** forms by direct S_N2 epoxide opening. Protonation of the resulting alkoxides gives the diols.
- **6.6** **C** and **D** are **constitutional positional isomers**.
- **6.7** The constitution of **C** has **three stereoisomers**: a trans enantiomeric pair and one cis meso form. The constitution of **D** has **four stereoisomers**: a trans enantiomeric pair and a cis enantiomeric pair. Thus there are **seven altogether**, listed explicitly below.

Solution

6.1 — Identification of A, B, C and D

The characteristic reversible dimerization identifies **A** as **cyclopenta-1,3-diene**. Its conjugated diene system readily undergoes a Diels–Alder reaction with another molecule of itself.

Peroxyacetic acid, $CC(=O)OO$, epoxidizes one double bond, producing **B**, cyclopentadiene monoepoxide, and acetic acid, $CC(=O)O$:



The reaction occurs at $20\text{ }^\circ\text{C}$ in dichloromethane, $ClCCl$. The neutral conditions preserve the epoxide for the subsequent hydrolysis. The two carbon–oxygen bonds of its three-membered ring lie on the same face of the five-membered carbon ring. Attack on either face of the achiral starting diene gives the two enantiomers of **B**.

Hydrolysis adds one molecule of water, O , to the epoxide:



This balanced equation applies separately to formation of **C** and **D**.

For **C**, put hydroxyl groups at positions 1 and 3 of a five-membered ring and the double bond between positions 4 and 5. Its carbon environments are:



Thus there are exactly **three different carbon environments**. The **trans** configuration has a proper twofold symmetry operation exchanging these carbon pairs, but is chiral. The corresponding cis configuration is meso. Consequently, the stated chirality identifies **C** as **trans-cyclopent-4-ene-1,3-diol**.

For **D**, the hydroxyl groups occupy adjacent positions 1 and 2, and the double bond occupies positions 3 and 4. All five carbons are different:

- The two hydroxyl-bearing carbons have different relationships to the double bond.

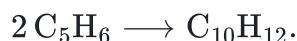
- The two alkene carbons have different neighbouring groups.
- The remaining carbon is a methylene carbon.

Direct anti opening of the epoxide gives **trans-cyclopent-3-ene-1,2-diol**.

To draw either observed diol, show one hydroxyl group on a solid wedge and the other on a dashed wedge. Reversing both wedges gives its enantiomer. Because the reagents and conditions are achiral, the products are racemic; the statement that **C** is chiral refers to its individual molecules.

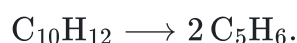
6.2 — Reaction used for separation

The dimerization is a **Diels–Alder reaction**. One molecule acts as the conjugated diene, and one double bond of another molecule acts as the dienophile:



Dimerization is achieved under the stated conditions: several hours at 100 °C, or heating to 140–150 °C under pressure.

Heating the isolated dimer to about 200 °C causes the reverse, **retro-Diels–Alder reaction**:



The regenerated volatile monomer is distilled off.

6.3 — Stereochemical rules

The relevant rules are:

1. **The diene must adopt an s-cis arrangement.** Cyclopentadiene already holds its conjugated double bonds in the required arrangement.
2. **The thermal cycloaddition is suprafacial on both components.** Both new bonds form on one face of the diene and on one face of the dienophile.
3. **Relative stereochemistry is retained.** Groups that are cis on the dienophile remain cis in the adduct.
4. **The endo arrangement is kinetically favoured.** The remaining unsaturated portion of the dienophile is directed toward the diene's developing bicyclic framework, allowing favourable secondary orbital interactions.

6.4 — Structure of the dimer

The product is **endo-dicyclopentadiene**, systematically **endo-tricyclo[5.2.1.0^{2,6}]deca-3,8-diene**. Its two enantiomeric SMILES are given in Answer 6.4.

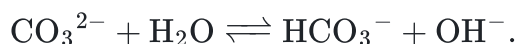
Its structure contains:

- A norbornene framework.
- A cyclopentene ring fused across the saturated two-carbon bridge.
- Two remaining carbon–carbon double bonds.
- An **endo** orientation of the annulated cyclopentene ring relative to the norbornene methylene bridge.

For a precise drawing using the tricyclic numbering, place double bonds at $C_3 = C_4$ and $C_8 = C_9$, and orient the annulated cyclopentene ring toward the one-carbon bridge.

6.5 — Mechanisms of formation of C and D

Carbonate ion, $[\text{O}^-]\text{C}(=\text{O})[\text{O}^-]$, supplies hydroxide ion, $[\text{OH}^-]$, through its equilibrium with water. Hydrogen carbonate ion is $\text{O}=\text{C}(\text{O})[\text{O}^-]$:



For the mechanism, label the carbon perimeter of **B** as

$$b_1 - b_2 = b_3 - b_4 - b_5 - b_1,$$

with the epoxide oxygen bridging b_1 and b_5 . Call the face bearing the epoxide oxygen the upper face.

Formation of C: allylic S_N2' opening

Three electron-pair movements occur together:

1. A hydroxide lone pair attacks b_3 from the lower face.
2. The π electrons of $b_2 = b_3$ form the new $b_1 = b_2$ double bond.
3. The $b_1 - \text{O}$ bond breaks, with its electrons moving onto the epoxide oxygen.

The original epoxide oxygen remains attached to b_5 as an alkoxide. The incoming hydroxyl group at b_3 is **trans** to it. Protonation gives **C**.

A representative intermediate is **trans-3-hydroxycyclopent-4-en-1-olate**:



The final ring has hydroxyl groups at positions 1 and 3 and its double bond at positions 4 and 5.

Formation of D: direct S_N2 opening

A hydroxide lone pair attacks the epoxide carbon b_1 from the lower face. Simultaneously, the $b_1 - \text{O}$ bond breaks toward oxygen.

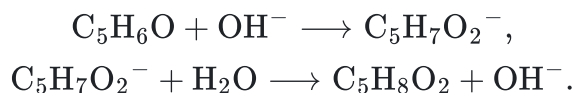
This gives inversion at the attacked carbon. The original epoxide oxygen remains attached to b_5 , so the two oxygen substituents are **trans**. The original $b_2 = b_3$ double bond remains in place.

A representative intermediate is **trans-2-hydroxycyclopent-3-en-1-olate**:

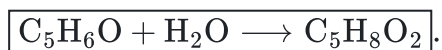


Protonation gives **D**.

For either pathway, the balanced steps are



In the proton-transfer step, the alkoxide oxygen takes a proton from water, and that water molecule's O–H bond electrons return to its oxygen. Hydroxide is therefore regenerated. The net reaction is



6.6 — Relationship between C and D

They are **constitutional isomers**, specifically **positional isomers**:

- **C** has the cyclopent-4-ene-1,3-diol connectivity.
- **D** has the cyclopent-3-ene-1,2-diol connectivity.

Their hydroxyl-bearing carbons have different connectivity relationships, so **C** and **D** are not stereoisomers of one another.

6.7 — All possible stereoisomers

For **C**, the two stereogenic centres are constitutionally equivalent. The nominal configurations (*1R*, *3S*) and (*1S*, *3R*) describe the same meso compound. Hence there are **three** stereoisomers.

Stereoisomer of cyclopent-4-ene-1,3-diol	Stereochemical SMILES	Character
trans-(<i>1R</i> , <i>3R</i>)	<chem>O[C@@H]1C[C@@H](O)C=C1</chem>	Chiral
trans-(<i>1S</i> , <i>3S</i>)	<chem>O[C@H]1C[C@H](O)C=C1</chem>	Enantiomer of the preceding form
cis-(<i>1R</i> , <i>3S</i>), identical to (<i>1S</i> , <i>3R</i>)	<chem>O[C@@H]1C[C@H](O)C=C1</chem>	Achiral, meso

The two trans forms are enantiomers. The cis meso form is a diastereomer of each trans form.

For **D**, the double bond makes the two stereogenic centres constitutionally inequivalent. No symmetry identifies any of the four configurations, so there are **four** stereoisomers.

Stereoisomer of cyclopent-3-ene-1,2-diol	Stereochemical SMILES	Character
trans-(<i>1R</i> , <i>2R</i>)	<chem>O[C@H]1[C@H](O)C=CC1</chem>	Chiral
trans-(<i>1S</i> , <i>2S</i>)	<chem>O[C@@H]1[C@@H](O)C=CC1</chem>	Enantiomer of the preceding form
cis-(<i>1R</i> , <i>2S</i>)	<chem>O[C@H]1[C@@H](O)C=CC1</chem>	Chiral
cis-(<i>1S</i> , <i>2R</i>)	<chem>O[C@@H]1[C@H](O)C=CC1</chem>	Enantiomer of the preceding form

Every cis form of **D** is a diastereomer of each trans form. There is no meso form of **D**.

In drawings, **cis** means both hydroxyl groups are on the same face; **trans** means they are on opposite faces. Ring conformations do not add further configurational stereoisomers.

$$N_C = 3, \quad N_D = 4, \quad N_{\text{total}} = 7.$$

The solution was checked against the official solution.

Problem 7: DNA: mass, coding capacity and base composition

Deoxyribonucleic acid (DNA) represents the genetic program of all living beings. The human genetic program is subdivided into 23 chromosomes.

7.1 Calculate the mass of a DNA thread in grams, which reaches from earth to the moon (340,000 km). A mass of 1 g represents 1,000 nucleotide pairs.

One nucleotide pair (base pair) has a length of 0.34 nm.

7.2 Give estimation on how many nucleotid pairs are stored in the chromosome set of a human being. Human cells can synthesize 50,000 different proteins, which are on the average 300 amino acids long. Only 2 % of the DNA code for proteins.

7.3 The DNA of the bacteriophage M13 shows the following base composition:

A: 23 %, T: 36 %, G: 21 %, C: 20 % (mole %)

What does the base composition tell about the structure of the DNA?

Official English text of the problem.

Answers

- **7.1:** $1 \times 10^{-3} \text{ g} = 1 \text{ mg}$, taking 1,000 nucleotide pairs to have a mass of 10^{-18} g .
- **7.2:** $\approx 2.3 \times 10^9$ nucleotide pairs in the 23-chromosome set; the unrounded estimate is 2.25×10^9 .
- **7.3:** M13 DNA is **single-stranded**: its base proportions are incompatible with a fully complementary double-stranded molecule.

Solution

7.1

The printed mass datum ("1 g") is a misprint; the intended value, also used in the official solution, is

$$m(1,000 \text{ nucleotide pairs}) = 10^{-18} \text{ g}.$$

Convert the Earth–Moon distance into nanometres:

$$L = 340,000 \text{ km} \times 10^{12} \frac{\text{nm}}{\text{km}} = 3.4 \times 10^{17} \text{ nm}.$$

Since each nucleotide pair contributes 0.34 nm to the length, the number of pairs is

$$N = \frac{3.4 \times 10^{17} \text{ nm}}{0.34 \text{ nm/pair}} = 1.0 \times 10^{18} \text{ pairs}.$$

Therefore,

$$m = (1.0 \times 10^{18} \text{ pairs}) \left(\frac{10^{-18} \text{ g}}{10^3 \text{ pairs}} \right) = 1 \times 10^{-3} \text{ g}.$$

7.2

Each amino acid is encoded by a codon of three nucleotides. Thus, a protein containing 300 amino acid residues requires approximately

$$300 \times 3 = 900$$

nucleotides on its coding strand, corresponding to **900 base pairs** of double-stranded DNA.

For 50,000 different proteins, the total coding requirement is

$$N_{\text{coding}} = 50,000 \times 300 \times 3 = 4.5 \times 10^7 \text{ base pairs}.$$

This represents $2\% = 0.02$ of the total DNA:

$$0.02N_{\text{total}} = 4.5 \times 10^7.$$

Hence,

$$N_{\text{total}} = \frac{4.5 \times 10^7}{0.02} = 2.25 \times 10^9 \approx \boxed{2.3 \times 10^9 \text{ base pairs}}.$$

This is the total across the stated 23 chromosomes. No additional factor of two is required: a base pair already includes the complementary nucleotides of both strands. Stop codons are neglected at the precision of this estimate.

7.3

The four base identities are listed below; the SMILES describe the free bases.

Symbol	Base	SMILES
A	Adenine	<chem>Nc1ncnc2[nH]cnc12</chem>
T	Thymine	<chem>Cc1c[nH]c(=O)[nH]c1=O</chem>
G	Guanine	<chem>Nc1nc2[nH]cnc2c(=O)[nH]1</chem>
C	Cytosine	<chem>Nc1cc[nH]c(=O)n1</chem>

In fully complementary double-stranded DNA, adenine pairs with thymine, and guanine pairs with cytosine. Counting both strands therefore requires

$$n_A = n_T, \quad n_G = n_C.$$

The supplied composition instead gives

$$x_A = 23\% \neq 36\% = x_T, \quad x_G = 21\% \neq 20\% = x_C.$$

In particular, the large difference between adenine and thymine is incompatible with a fully complementary duplex. The intended structural conclusion is therefore

M13 DNA is single-stranded.

The composition alone does not determine whether the strand is circular or linear. A complete DNA SMILES cannot be specified from these percentages: its nucleotide sequence and connectivity are missing. SMILES also does not specify its three-dimensional conformation.

The solution was checked against the official solution.

Problem 8: Amino acid sequence of a pain-relieving peptide

The sequence of the amino acids in a peptide can be determined by a combination of chemical and enzymatic methods. The peptide in question functions in the human body as a pain reliever.

a) Hydrolysis of the peptide in 6 M HCl at 110°C followed by an analysis of the liberated amino acids, resulted in a molar ratio of Gly, Leu, and aromatic amino acids Phe, Tyr 2 : 1 : 1 : 1.

b) Reacting the peptide with 2,4-dinitrofluorobenzene (DNFB), followed by hydrolysis and chromatographic analysis, yielded the tyrosine derivative.

c) Partial hydrolysis with chymotrypsin yielded Leu, Tyr and a smaller peptide. After hydrolysis of this peptide Gly and Phe were identified in a ratio 2 : 1. Chymotrypsin is a protease which cleaves a peptide bond following an aromatic amino acid.

Problems:

8.1 Determine the amino acid sequence from the given information.

8.2 Write the structural formula of the DNFB- and the dansyl derivative of tyrosine. What is the advantage of the dansylation in comparison to the DNFB-modification?

Dansyl means 5-N,N-dimethylaminonaphtalene-4-sulphonyl.

8.3 In a similar peptide which shows the same biological activity, leucine is replaced by methionine. Explain from the chemical structure of both amino acids why the replacement is possible without loss of biological activity.

Official English text of the problem.

Answers

- **8.1** The sequence, from the N-terminus to the C-terminus, is **Tyr–Gly–Gly–Phe–Leu**, called **Leu-enkephalin**.

SMILES: N[C@@H](Cc1ccc(O)cc1)C(=O)NCC(=O)NCC(=O)N[C@@H](Cc1ccccc1)C(=O)N[C@@H](CC(C)C)C(=O)O

- **8.2** The N-terminal sequencing derivatives are:

***N*^α-(2,4-dinitrophenyl)-L-tyrosine**, with a direct bond between the tyrosine amino nitrogen and the dinitrophenyl ring.

SMILES: N(c1ccc([N+](=O)[O-])cc1[N+](=O)[O-])[C@@H](Cc1ccc(O)cc1)C(=O)O

***N*^α-dansyl-L-tyrosine**, with a sulfonamide linkage. Using the conventional definition of dansyl:

SMILES: CN(C)c1cccc2c(S(=O)(=O)N[C@@H](Cc3ccc(O)cc3)C(=O)O)cccc12

Dansyl derivatives are **strongly fluorescent**, permitting much more sensitive detection and therefore sequencing with smaller quantities of peptide. The printed dansyl locants are addressed below.

- **8.3 L-Leucine**, N[C@@H](CC(C)C)C(=O)O, and **L-methionine**, N[C@@H](CCSC)C(=O)O, have uncharged, predominantly hydrophobic side chains of comparable bulk. Their substitution can therefore preserve the interactions required for biological activity.

Solution

8.1 — Determination of the sequence

The amino-acid composition is:

Residue	Number in the pentapeptide	Free amino acid: name and SMILES
Gly	2	Glycine: <chem>NCC(=O)O</chem>
Leu	1	L-Leucine: <chem>N[C@@H](CC(C)C)C(=O)O</chem>
Phe	1	L-Phenylalanine: <chem>N[C@@H](Cc1ccccc1)C(=O)O</chem>
Tyr	1	L-Tyrosine: <chem>N[C@@H](Cc1ccc(O)cc1)C(=O)O</chem>

DNFB reacts with the free **N-terminal amino group**. The identification of its tyrosine derivative after hydrolysis therefore places **Tyr at the N-terminus**.

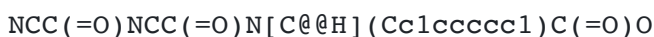
Chymotrypsin cleaves on the C-terminal side of an aromatic residue. Here the aromatic residues are Tyr and Phe.

1. Cleavage immediately after the N-terminal Tyr releases free Tyr.
2. Free Leu must be the **C-terminal residue**: an internal Leu could not be released as a single amino acid because this would require cleavage after Leu, contrary to the stated specificity.
3. Consequently, the bond immediately before the terminal Leu must follow an aromatic residue. Tyr is already at the N-terminus, so this residue is Phe.
4. The remaining fragment contains two Gly and one Phe. Since Phe must end this fragment, its order is **Gly–Gly–Phe**.

Thus the cleavage pattern is



The smaller peptide is **glycylglycyl-L-phenylalanine**:



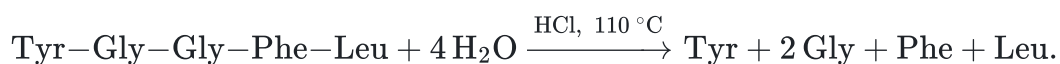
Each hydrolysed peptide bond consumes one molecule of **water**, H_2O . Using sequence abbreviations for peptides with free termini, the balanced enzymatic hydrolysis is



Hydrolysis of the smaller peptide gives



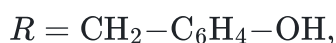
in agreement with the observed 2 : 1 ratio. Complete hydrolysis of the original peptide breaks four peptide bonds:



These balances use neutral molecular forms; the amino groups are protonated in the strongly acidic hydrolysis mixture.

8.2 – Structures and advantage of dansylation

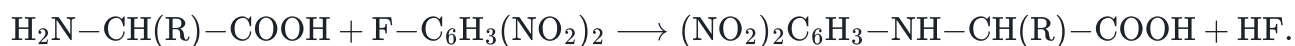
Let R denote the tyrosine side chain,



with the phenolic OH **para** to the CH_2 group.

DNFB derivative. The reagent is **1-fluoro-2,4-dinitrobenzene**, Fc1ccc([N+](=O)[O-])cc1[N+](=O)[O-].

The amino nitrogen replaces fluorine by nucleophilic aromatic substitution. The neutral-form reaction is



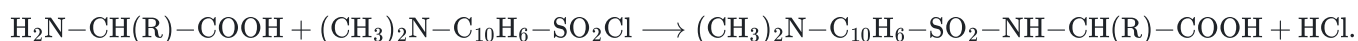
The formal by-product is **hydrogen fluoride**, F; base neutralizes it during derivatization.

To draw the product, attach the tyrosine amino nitrogen directly to carbon 1 of a benzene ring bearing nitro groups at **positions 2 and 4**. The nitrogen retains one hydrogen, and the tyrosine phenolic hydroxyl remains present in this N^α -labelled structure.

Dansyl derivative. Conventional **dansyl chloride**, or **5-(dimethylamino)naphthalene-1-sulfonyl chloride**, has SMILES:

```
CN(C)c1cccc2c(S(=O)(=O)Cl)cccc12
```

The amino nitrogen replaces chlorine at sulfur, forming a sulfonamide:



The formal by-product is **hydrogen chloride**, Cl, which is likewise neutralized by base.

To draw conventional dansyltyrosine, place the dimethylamino group at naphthalene carbon **5** and the sulfonyl group at carbon **1**. The latter has two S=O bonds and an S—NH bond to the tyrosine amino nitrogen.

In peptide sequencing, these reactions label the N-terminal nitrogen while the residue is still part of the peptide. Subsequent hydrolysis releases the labelled amino acid.

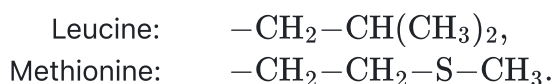
The advantage of dansylation is its **strong fluorescence**, allowing detection at much lower concentrations than the coloured dinitrophenyl derivatives.

The statement instead specifies **5-(dimethylamino)naphthalene-4-sulphonyl**. Taken literally, this gives a different positional isomer, with the two substituents in peri positions. The corresponding N^α -**[5-(dimethylamino)naphthalene-4-sulfonyl]-L-tyrosine** is:

```
CN(C)c1cccc2cccc(S(=O)(=O)N[C@@H](Cc3ccc(O)cc3)C(=O)O)c12
```

8.3 — Why methionine can replace leucine

The side chains are



Both are flexible, predominantly hydrophobic groups of comparable size. Methionine contains an **uncharged thioether**, which does not introduce a charged side chain.

The substitution preserves the peptide backbone and can maintain similar hydrophobic contacts at the receptor. Thus it is chemically reasonable that replacing the terminal leucine with methionine retains the pain-relieving activity.

The solution was checked against the official solution.