

IChO 2015

Theory problems and solutions · Baku, Azerbaijan · 8 theory problems with complete solutions

eulersolve.org/icho/2015/

Problem 1: New and well-forgotten old refrigerants

The problem of choosing a refrigerant for refrigeration and air conditioning systems attracted the attention of scientists and technologists throughout the last century. It has been suggested that during this time refrigerants progressed through four generations.

Ammonia, which was ascribed to the first generation, had been used in most of the oldest refrigeration units. It was later replaced by chlorofluorocarbons (CFCs) – derivatives of methane and ethane with the hydrogen atoms replaced by fluorine and chlorine.

In Baku, at "Bakkonditsioner" factory, production of the first Soviet serial household air conditioners BK-1500 had been launched. A second-generation refrigerant chlorodifluoromethane CHF_2Cl was used in them. In this problem, we compare various refrigerants in terms of thermodynamics.



First air conditioner of Baku factory in souvenir shop in the Old City ("Icheri Sheher").

First air conditioner of Baku factory in souvenir shop in the Old City ("Icheri Sheher").

Thermodynamic properties of various refrigerants:

Refrigerant	"Generation"	$\Delta H_{\text{vap}}/\text{kJ mol}^{-1}$ (at 280 K)	$C_{V(\text{gas})}/\text{J K}^{-1} \text{mol}^{-1}$
NH_3	1	21.3	26.7

Table continued:

CHF_2Cl	2	20.0	48.8
$\text{CF}_3\text{CH}_2\text{F}$	3	22.1	79
$\text{CF}_3\text{CF}=\text{CH}_2$	4	19.1	120

Consider a model refrigeration cycle consisting of 4 steps schematically shown below in the pressure (p) – internal energy (U) coordinates.

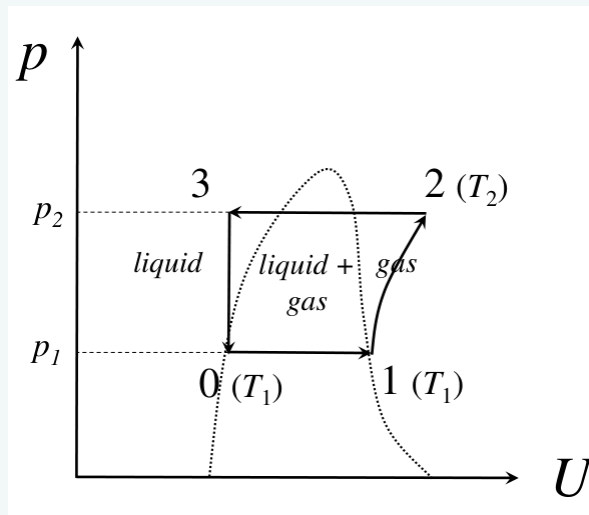


Diagram 1. Dashed line indicates the phase boundaries

During the first step of the cycle (line 0-1 in diagram 1), a liquid refrigerant is boiling at constant pressure p_1 and temperature T_1 (boiling temperature) until it completely evaporates. At this step, the refrigeration unit absorbs heat from surrounding objects. At the second step, the refrigerant undergoes reversible adiabatic compression and heats up to temperature T_2 (line 1-2). After that the compressed refrigerant is cooled in a condenser at constant pressure p_2 (line 2-3) and then returns to the initial state (line 3-0).

Let the cycle involve 1 mole of refrigerant, which is initially (point 0) completely liquid, $T_1 = 280 \text{ K}$, $T_2 = 380 \text{ K}$, assume that the vapor of any refrigerant behaves like an ideal gas. The thermodynamic characteristics of refrigerants are listed in the table above.

1.1 For each of refrigerants, ammonia and chlorodifluoromethane, calculate the amount of heat Q absorbed by refrigeration unit during heat exchange (line 0-1) and the work W required to compress its vapor adiabatically (line 1-2).

1.2. Which quantity(ies) remain(s) constant during the adiabatic compression step? Indicate by the circle(s).

$U \quad H \quad S \quad G \quad V$

To compare the energy efficiency of refrigeration cycles with different parameters and refrigerants, the coefficient of performance (COP) is used, which is defined as a ratio of heat removed from a cooled system to the work of compressor: $COP = Q/W$.

1.3 Calculate the values of COP in a considered cycle for ammonia and chlorodifluoromethane.

1.4 Why was ammonia replaced by CFCs in household refrigeration units? (Choose only one option)

- a) to increase the energy efficiency of refrigeration cycles,
- b) because the density of ammonia is less than that of air under the same conditions,
- c) for user safety reasons.

A search for replacement of CFCs as refrigerants started when it was shown that their use can cause irreparable damage to the protective ozone layer of the atmosphere. The third, ozone-friendly generation of refrigerants came on the scene. Its typical representatives are fluoroalkanes.

1.5 What is the cause of the damage made by CFCs to the ozone layer? (Choose only one option.)

- a) Ozone molecule easily adds to C—F bond,
- b) C—F bond is easily broken by radiation, which leads to the formation of free radicals,
- c) ozone molecule easily adds to C—Cl bond,
- d) C—Cl bond is easily broken by radiation, which leads to the formation of free radicals.

1.6 However, under the 1997 Kyoto Protocol, fluoroalkanes also had to be replaced because they accumulate in the atmosphere and rapidly absorb infrared radiation, causing a rise in temperature of the atmosphere (the greenhouse effect). The refrigerants of the fourth generation such as 2,3,3,3-tetrafluoropropene $\text{CF}_3\text{CF}=\text{CH}_2$ have been suggested and are coming into use. Why does this compound enhance the greenhouse effect less than fluoroalkanes? (Choose only one option)

- a) It is more reactive and easier to decompose,
- b) it easily reacts with ozone,
- c) it is better soluble in water.

1.7 Calculate the values of the *COP* in the refrigeration cycle considered above for two refrigerants of the third and fourth generations – $\text{CF}_3\text{CH}_2\text{F}$ and $\text{CF}_3\text{CF}=\text{CH}_2$. Did the energy efficiency improve in comparison with CHF_2Cl ? Choose "Yes" or "No".

Unlike household appliances, industrial refrigeration systems are often still using ammonia. It does not contribute to the greenhouse effect nor does it destroy the ozone layer. Industrial units can have a huge size and a large cost. Prior to their construction, they should be carefully modeled taking into account many different factors. In real systems, some part of the refrigerant at the start of the heat exchange with the environment is in the vapor phase (point 0 in the diagram below), and at the end (point 1) it is always overheated above the boiling point.

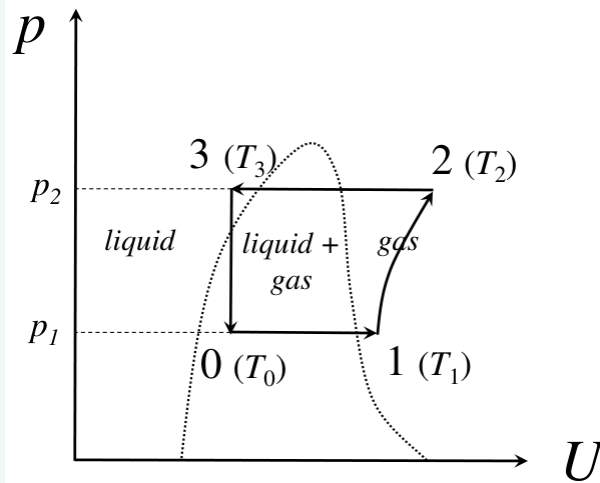


Diagram 2. Dashed line indicates the phase boundaries

Consider a cycle with 1 mole of ammonia. Its thermodynamic properties are the following: enthalpy of vaporization $\Delta H_{\text{vap}} = 23.35 \text{ kJ mol}^{-1}$ at $T_{\text{vap}} = 239.8 \text{ K}$ (boiling temperature at 1 bar pressure). Heat capacity of the liquid phase $C_{V(\text{liq})} = 77 \text{ J K}^{-1} \text{ mol}^{-1}$, of the gas phase $C_{V(\text{gas})} = 26.7 \text{ J K}^{-1} \text{ mol}^{-1}$. Assume that the heat capacities are temperature-independent and the vapor behaves like an ideal gas. The temperature dependence of the saturated vapor pressure of ammonia can be described by the empirical equation

$$\log(p/\text{bar}) = 4.87 - 1114/(T/\text{K} - 10.4).$$

During the first step of the cycle (line 0-1 in diagram 2), the equilibrium mixture of liquid refrigerant and its vapor receives heat from the environment at constant pressure $p_1 = 3.0 \text{ bar}$. The refrigerant completely evaporates and overheats up to the temperature $T_1 = 275 \text{ K}$. In the beginning of the process (point 0), the molar fraction of gaseous ammonia is $x = 0.13$.

1.8 Calculate the initial temperature of refrigerant T_0 , its volume change ΔV and the amount of heat Q absorbed by refrigeration unit during this step. Take into account that the dependence of ΔH_{vap} from the temperature **cannot** be neglected. Then the refrigerant is reversibly and adiabatically compressed. It heats up to the temperature $T_2 = 393 \text{ K}$ (line 1-2).

1.9 Find the work W required for compression and the COP of the system. If you were not able to find Q in 4.1, use $Q = 20.15 \text{ kJ}$.

At the next step corresponding to the line 2-3 in diagram, the compressed refrigerant is cooled in a condenser at constant pressure. Then it returns to the initial state through adiabatic expansion with zero work (line 3-0).

1.10 Determine the temperature T_3 at point 3 to which the refrigerant is cooled in a condenser.

In the production of refrigeration units it is necessary to consider climatic factors. If a condenser is cooled by atmospheric air, the temperature T_3 increases as the air temperature increases.

1.11 How will the COP change if T_3 increases while T_0, T_1, T_2 remain the same?

- a) increase,
- b) remain the same,
- c) decrease.

Answers

- **1.1** Ammonia, NH_3 , SMILES `N`: $Q = 21.3 \text{ kJ}$, $W = 2.67 \text{ kJ}$. Chlorodifluoromethane, CHF_2Cl , SMILES `FC(F)Cl`: $Q = 20.0 \text{ kJ}$, $W = 4.88 \text{ kJ}$.
- **1.2** Circle *S* only.
- **1.3** $\text{COP}_{\text{NH}_3} = 7.98$; $\text{COP}_{\text{CHF}_2\text{Cl}} = 4.10$.
- **1.4 c)** For user safety reasons.
- **1.5 d)** Radiation breaks $\text{C}-\text{Cl}$ bonds, forming free radicals.
- **1.6 a)** It is more reactive and easier to decompose.
- **1.7** 1,1,1,2-Tetrafluoroethane, $\text{CF}_3\text{CH}_2\text{F}$, SMILES `FCC(F)(F)F`: $\text{COP} \approx 2.80$, **No.** 2,3,3,3-Tetrafluoroprop-1-ene, $\text{CF}_3\text{CF}=\text{CH}_2$, SMILES `C=C(F)C(F)(F)F`: $\text{COP} \approx 1.59$, **No.**
- **1.8** $T_0 \approx 264 \text{ K}$, $\Delta V \approx +6.67 \text{ L}$, $Q \approx 19.82 \text{ kJ}$.
- **1.9** $W \approx 3.15 \text{ kJ}$, $\text{COP} \approx 6.29$.
- **1.10** $T_3 \approx 298 \text{ K}$.
- **1.11 c)** Decrease.

Solution

Take $W > 0$ to mean work supplied to the refrigerant, and use

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

All numerical heat and work values refer to the stated $n = 1 \text{ mol}$. For the liquid, use the implicit approximation of negligible volume and incompressibility, so that its internal energy is pressure-independent and $C_{p,\text{liq}} \simeq C_{V,\text{liq}}$.

1.1

During constant-pressure vaporization, the heat absorbed equals the enthalpy change:

$$Q = n\Delta H_{\text{vap}}.$$

During adiabatic compression, $q = 0$. The first law therefore gives

$$W = \Delta U = nC_{V,\text{gas}}(T_2 - T_1).$$

Here,

$$T_2 - T_1 = 380 - 280 = 100 \text{ K}.$$

Thus:

Refrigerant	Heat absorbed Q	Compression work W
Ammonia, NH_3	21.3 kJ	$(1 \text{ mol})(26.7 \text{ J mol}^{-1} \text{ K}^{-1})(100 \text{ K}) = 2.67 \text{ kJ}$
Chlorodifluoromethane, CHF_2Cl	20.0 kJ	$(1 \text{ mol})(48.8 \text{ J mol}^{-1} \text{ K}^{-1})(100 \text{ K}) = 4.88 \text{ kJ}$

1.2

The compression is both reversible and adiabatic. Consequently,

$$dS = \frac{\delta q_{\text{rev}}}{T} = 0.$$

Therefore, **circle S only**.

The temperature increase causes U and H to increase, compression decreases V , and G is not conserved.

1.3

By definition,

$$\text{COP} = \frac{Q}{W}.$$

For ammonia,

$$\text{COP}_{\text{NH}_3} = \frac{21.3}{2.67} = 7.98.$$

For chlorodifluoromethane,

$$\text{COP}_{\text{CHF}_2\text{Cl}} = \frac{20.0}{4.88} = 4.10.$$

The coefficients of performance are dimensionless.

1.4

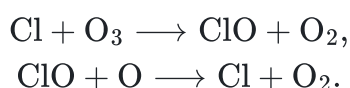
The correct choice is **c), for user safety reasons**.

Ammonia is toxic and strongly irritating, so leakage into occupied rooms is hazardous. The replacement refrigerants offered better safety for household use. The calculated coefficients of performance do not support increased energy efficiency as the reason for replacement.

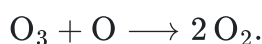
1.5

The correct choice is **d)**.

Ultraviolet radiation can cleave $\text{C}-\text{Cl}$ bonds homolytically: one bonding electron goes to each fragment, producing a chlorine radical. Chlorine radicals participate in catalytic ozone-destruction cycles, for example



Adding these equations gives



Chlorine is regenerated, allowing it to destroy additional ozone molecules.

The species in this cycle are chlorine atom/radical, SMILES `[Cl]`; ozone, SMILES `[O-][O+]=O` (one resonance representation); chlorine monoxide radical, SMILES `[O]Cl`; dioxygen, SMILES `O=O`; and atomic oxygen, SMILES `[O]`. The equations express the catalytic sequence; the homolytic electron movement is described above.

1.6

The correct choice is **a)**.

2,3,3,3-Tetrafluoroprop-1-ene, $\text{C}=\text{C}(\text{F})\text{C}(\text{F})(\text{F})\text{F}$, contains a carbon-carbon double bond that provides a reactive site for atmospheric degradation. Its shorter atmospheric lifetime limits its accumulation and therefore reduces its contribution to the greenhouse effect.

No *E/Z* designation is possible for this alkene because one carbon of the double bond bears two hydrogen atoms.

1.7

For each refrigerant in the first model cycle,

$$\text{COP} = \frac{n\Delta H_{\text{vap}}}{nC_{V,\text{gas}}(T_2 - T_1)}.$$

For 1,1,1,2-tetrafluoroethane,

$$W = (1 \text{ mol})(79 \text{ J mol}^{-1} \text{ K}^{-1})(100 \text{ K}) = 7.9 \text{ kJ},$$

$$\text{COP}_{\text{CF}_3\text{CH}_2\text{F}} = \frac{22.1}{7.9} \approx 2.80.$$

For 2,3,3,3-tetrafluoroprop-1-ene,

$$W = (1 \text{ mol})(120 \text{ J mol}^{-1} \text{ K}^{-1})(100 \text{ K}) = 12.0 \text{ kJ},$$

$$\text{COP}_{\text{CF}_3\text{CF}=\text{CH}_2} = \frac{19.1}{12.0} \approx 1.59.$$

Both values are below the value 4.10 for chlorodifluoromethane. Thus, select **"No" for both refrigerants.**

1.8

Initially, the liquid and vapor are in equilibrium, so T_0 is the saturation temperature at 3.0 bar. Taking the empirical logarithm as base 10,

$$\log_{10}(3.0) = 4.87 - \frac{1114}{T_0/\text{K} - 10.4}.$$

Hence,

$$T_0 = \left(10.4 + \frac{1114}{4.87 - \log_{10}(3.0)} \right) \text{K} = 263.992 \text{ K}.$$

Therefore,

$$T_0 \approx 264 \text{ K}.$$

Initially, $xn = 0.13 \text{ mol}$ is gaseous. Neglecting the liquid volume,

$$V_0 = \frac{xnRT_0}{p_1}.$$

At point 1, all the refrigerant is gaseous:

$$V_1 = \frac{nRT_1}{p_1}.$$

Using $p_1 = 3.0 \times 10^5 \text{ Pa}$,

$$V_0 = 0.951 \text{ L}, \quad V_1 = 7.621 \text{ L}.$$

Thus,

$$\Delta V = \frac{nR(T_1 - xT_0)}{p_1} = 6.670 \times 10^{-3} \text{ m}^3,$$

$$\boxed{\Delta V \approx +6.67 \text{ L.}}$$

To calculate the heat, first correct the enthalpy of vaporization to T_0 . For the ideal gas,

$$C_{p,\text{gas}} = C_{V,\text{gas}} + R = 35.014 \text{ J mol}^{-1} \text{ K}^{-1}.$$

Using $C_{p,\text{liq}} \simeq 77 \text{ J mol}^{-1} \text{ K}^{-1}$, Kirchhoff's relation gives

$$\Delta H_{\text{vap}}(T_0) = \Delta H_{\text{vap}}(T_{\text{vap}}) + (C_{p,\text{gas}} - C_{p,\text{liq}})(T_0 - T_{\text{vap}}).$$

Numerically,

$$\begin{aligned} \Delta H_{\text{vap}}(T_0) &= 23.35 \text{ kJ mol}^{-1} \\ &\quad + (-0.041986 \text{ kJ mol}^{-1} \text{ K}^{-1})(263.992 - 239.8) \text{ K} \\ &= 22.334 \text{ kJ mol}^{-1}. \end{aligned}$$

Only the initially liquid fraction, $1 - x = 0.87$, must evaporate. Afterwards, the entire mole of vapor is heated from T_0 to T_1 . At constant pressure,

$$Q = n(1 - x)\Delta H_{\text{vap}}(T_0) + nC_{p,\text{gas}}(T_1 - T_0).$$

Therefore,

$$\begin{aligned} Q &= (0.87 \text{ mol})(22.334 \text{ kJ mol}^{-1}) \\ &\quad + (1 \text{ mol})(0.035014 \text{ kJ mol}^{-1} \text{ K}^{-1})(275 - 263.992) \text{ K} \\ &= 19.816 \text{ kJ}. \end{aligned}$$

Thus,

$$\boxed{Q \approx 19.82 \text{ kJ.}}$$

As an independent energy-balance check,

$$\Delta U_{0 \rightarrow 1} = 17.815 \text{ kJ}, \quad p_1 \Delta V = 2.001 \text{ kJ},$$

so $Q = \Delta U_{0 \rightarrow 1} + p_1 \Delta V = 19.816 \text{ kJ}$.

1.9

For the adiabatic compression,

$$W = \Delta U = nC_{V,\text{gas}}(T_2 - T_1).$$

Thus,

$$W = (1 \text{ mol})(26.7 \text{ J mol}^{-1} \text{ K}^{-1})(393 - 275) \text{ K} = 3150.6 \text{ J}.$$

Therefore,

$$\boxed{W \approx 3.15 \text{ kJ,}}$$

$$\boxed{\text{COP} = \frac{19.816}{3.1506} \approx 6.29.}$$

Using the supplied fallback $Q = 20.15 \text{ kJ}$ would instead give $\text{COP} \approx 6.40$.

1.10

For the specified return step $3 \rightarrow 0$, both heat and work are zero. Therefore,

$$U_0 - U_3 = q_{3 \rightarrow 0} + w_{3 \rightarrow 0} = 0,$$

so

$$U_3 = U_0.$$

At point 3 the refrigerant is liquid. At point 0 it contains a vapor fraction x , so its internal energy is

$$U_0 = nU_{m,\text{liq}}(T_0) + nx\Delta U_{\text{vap}}(T_0).$$

Consequently,

$$nC_{V,\text{liq}}(T_3 - T_0) = nx\Delta U_{\text{vap}}(T_0).$$

Neglecting liquid volume and treating the vapor as ideal,

$$\Delta U_{\text{vap}}(T_0) = \Delta H_{\text{vap}}(T_0) - RT_0.$$

Thus,

$$\Delta U_{\text{vap}}(T_0) = 22.334 - \frac{8.314(263.992)}{1000} = 20.139 \text{ kJ mol}^{-1}.$$

It follows that

$$T_3 = T_0 + \frac{x\Delta U_{\text{vap}}(T_0)}{C_{V,\text{liq}}},$$

$$T_3 = 263.992 \text{ K} + \frac{0.13(20139 \text{ J mol}^{-1})}{77 \text{ J mol}^{-1} \text{ K}^{-1}} = 297.994 \text{ K}.$$

Therefore,

$$\boxed{T_3 \approx 298 \text{ K}.}$$

1.11

The correct choice is **c), decrease**.

At fixed T_0 , the energy balance for the return step gives

$$x = \frac{C_{V,\text{liq}}(T_3 - T_0)}{\Delta U_{\text{vap}}(T_0)}.$$

Increasing T_3 therefore increases the initial vapor fraction x . This fraction is no longer fixed at 0.13.

The heat absorbed is

$$Q = n(1 - x)\Delta H_{\text{vap}}(T_0) + nC_{p,\text{gas}}(T_1 - T_0).$$

With T_0 and T_1 fixed, increasing x reduces Q , because less liquid remains available to evaporate.

Meanwhile,

$$W = nC_{V,\text{gas}}(T_2 - T_1)$$

remains constant because T_1 and T_2 are unchanged. Hence,

$$\boxed{\text{COP} = Q/W \text{ decreases}.}$$

The solution was checked against the official solution.

Problem 2: Coupling of chemical reactions



I. Prigogine (left)



N. Shilov



W. Ostwald

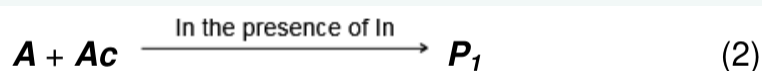
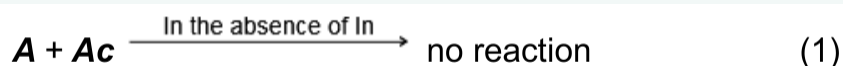
When in the system one reaction allows another one to proceed they say that these two reactions are coupled. Ilya Prigogine, Nobel prize winner in chemistry (1977) in his books widely used the concept of "coupled reactions". Coupling of reactions is an essential feature of living systems, including human body.

How one reaction makes another one to occur? In this problem we are going to discuss several possible mechanisms of coupling.

(I) "Chemical coupling"

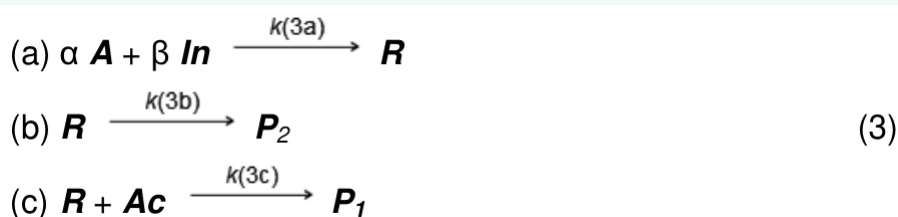
"On Chemical coupling" was the title of the dissertation defended by Russian chemist N. Shilov in 1905. N. Shilov was the graduate student of famous professor W. Ostwald. Dr. Shilov described the following set of reactions.

The substance A does not react with Ac . In the presence of the third reagent (called inductor), In , however, the reaction of A with Ac takes place:



In is not a catalyst! Its concentration decreases in the course of the reactions.

According to the scheme proposed by Shilov, Ac reacts not with A itself, but with the intermediate product R of the reaction of A with In . There is another, competing reaction of R that forms P_2 .



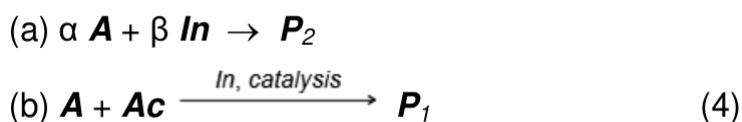
α and β are stoichiometric coefficients. Other stoichiometric coefficients and reaction order with respect to all reactants in all three reactions are unity.

In the Shilov's experiments the ratio of the consumed amounts of Ac and In , $I = \Delta n_{Ac} / \Delta n_{In}$ increased up to the constant value with the increasing initial concentration $[Ac]_0$ at $[In]_0 = \text{const}$.

2.1 What was this limiting constant value of I at $[Ac]_0 \rightarrow \infty$, $[In]_0 = \text{const}$?

2.2 Derive an expression for I using the steady-state approximation if necessary. Plot the graph of I vs $[In]_0$ at $[Ac]_0 = \text{const}$. Assume that In was completely consumed and Ac was in excess..

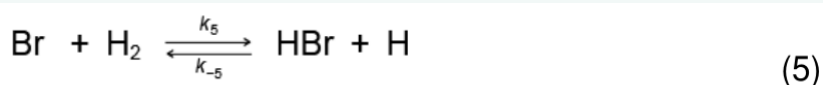
If Shilov's mechanism is not valid and In is a conventional catalyst of the reaction (2) then In reacts simultaneously with A and its concentration decreases. The reaction scheme in this case is as follows:



2.3 What is the limiting value of I for the reaction scheme (4) at $[Ac]_0 \rightarrow \infty$, $[In]_0 = \text{const}$?

(II) "Kinetic coupling"

The standard Gibbs energy of the gas-phase reaction

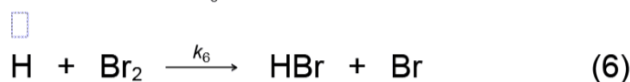
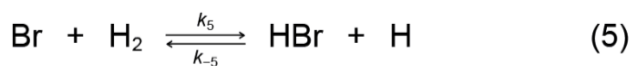


is positive, $\Delta G^\circ(5) = 66 \text{ kJ mol}^{-1}$ at $T = 600 \text{ K}$.

2.4 What is the ratio of the rates of forward and reverse reactions, r_5/r_{-5} , at this temperature, standard pressures of H_2 and HBr and equal pressures of H and Br ?

(If you could not answer this question, for further calculations use reference value $r_5/r_{-5} = 3.14 \times 10^{-7}$.)

Reaction (5) proceeds in the forward direction due to the reaction (6) which simultaneously occurs in the system:



k_5 , k_{-5} , k_6 are rate constants of forward and reverse reaction (5) and forward reaction (6), respectively.

This is the kinetic coupling of two reactions.

Let pressures of neutral molecules keep standard values $p(\text{H}_2) = p(\text{Br}_2) = p(\text{HBr}) = 1$ bar, and pressures of radicals $p(\text{H})$, $p(\text{Br})$ reach steady-state values. Rate constant k_6 is 10 times larger than k_{-5} .

2.5 Calculate $\Delta G(5)$ and r_5/r_{-5} under such conditions.

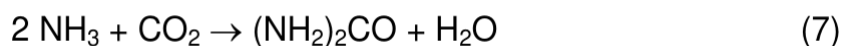
(III) "Second law of thermodynamics restricts coupling"

According to the Second Law of thermodynamics, two simultaneously occurring chemical reactions should decrease the system's Gibbs energy G_{syst} ,

$$\frac{\Delta G_{\text{syst}}}{\Delta t} < 0$$

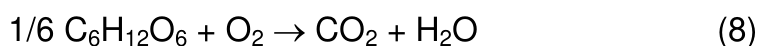
One of these reactions may have positive Gibbs energy and still proceed in the forward direction due to the coupling with the second reaction. This second reaction must have negative Gibbs energy and the requirements of the Second law must be fulfilled! Consider the example.

The synthesis of urea under specific conditions



$$(\Delta G(7) = 46.0 \text{ kJ mol}^{-1})$$

is supposed to be coupled with the complete oxidation of glucose (under the same conditions)



$$\Delta G(8) = -481.2 \text{ kJ mol}^{-1},$$

$$r(8) = 6.0 \times 10^{-8} \text{ mol dm}^{-3} \text{ min}^{-1}.$$

Both reactions are presented schematically. No other reactions are considered.

2.6 What is the maximum rate of the reaction (7) permitted by the Second Law if this reaction is coupled to reaction (8)?

Answers

- **2.1:** $I_{\text{lim}} = \frac{1}{\beta}$.
- **2.2:** With excess Ac , so that $[Ac] \approx [Ac]_0$,

$$I \approx \frac{k(3c)[Ac]_0}{\beta(k(3b) + k(3c)[Ac]_0)}.$$

The graph against $[In]_0$ is horizontal within this approximation.

- **2.3:** $I \rightarrow \infty$ in the intended first-order catalytic model.
- **2.4:** $\frac{r_5}{r_{-5}} = 1.8 \times 10^{-6}$.
- **2.5:** $\frac{r_5}{r_{-5}} = 11$, $\Delta G(5) = -12.0 \text{ kJ mol}^{-1}$.
- **2.6:** The upper limiting rate is

$$r_{7,\text{lim}} = 6.3 \times 10^{-7} \text{ mol dm}^{-3} \text{ min}^{-1}.$$

Strict decrease of Gibbs energy requires a rate below the unrounded bound.

Solution

The symbols A , Ac , In , R , P_1 , P_2 represent unspecified substances. In particular, Ac and In are labels here, not the elements actinium and indium. Their structures and SMILES cannot be assigned from the information provided.

2.1

Each occurrence of reaction (3a) consumes β units of In and produces one unit of the intermediate R . That intermediate either forms P_2 , consuming no Ac , or forms P_1 , consuming one unit of Ac .

Consequently, after all the intermediate has reacted,

$$\Delta n_{In} = \beta(n_{P_1} + n_{P_2}), \quad \Delta n_{Ac} = n_{P_1}.$$

Thus

$$I = \frac{1}{\beta} \frac{n_{P_1}}{n_{P_1} + n_{P_2}} \leq \frac{1}{\beta}.$$

As $[Ac]_0 \rightarrow \infty$, capture of R by Ac overwhelmingly outcompetes formation of P_2 . Therefore,

$$I_{\text{lim}} = \frac{1}{\beta}.$$

2.2

Write

$$k_a = k(3a), \quad k_b = k(3b), \quad k_c = k(3c).$$

Because the stated reaction orders are unity, the rates of the three steps are

$$v_a = k_a[A][In], \quad v_b = k_b[R], \quad v_c = k_c[R][Ac].$$

The stoichiometric coefficients α and β do not become exponents in these rate laws.

The steady-state approximation for the intermediate gives

$$\frac{d[R]}{dt} = k_a[A][In] - k_b[R] - k_c[R][Ac] \approx 0,$$

hence

$$[R] \approx \frac{k_a[A][In]}{k_b + k_c[Ac]}.$$

The consumption rates are

$$-\frac{d[In]}{dt} = \beta k_a[A][In]$$

and

$$-\frac{d[Ac]}{dt} = k_c[Ac][R] \approx \frac{k_c[Ac] k_a[A][In]}{k_b + k_c[Ac]}.$$

Their ratio is therefore

$$\frac{-d[Ac]/dt}{-d[In]/dt} \approx \frac{k_c[Ac]}{\beta(k_b + k_c[Ac])}.$$

With Ac in sufficient excess to take $[Ac] \approx [Ac]_0$, this ratio is constant throughout the reaction. Integrating, and using complete consumption of In , gives

$$\Delta[Ac] \approx \frac{k_c[Ac]_0}{\beta(k_b + k_c[Ac]_0)} [In]_0.$$

At fixed volume, the concentration-consumption ratio equals the amount-consumption ratio, so

$$I \approx \frac{k_c[Ac]_0}{\beta(k_b + k_c[Ac]_0)} = \frac{1}{\beta} \frac{[Ac]_0}{k_b/k_c + [Ac]_0}.$$

This expression approaches $1/\beta$ as $[Ac]_0 \rightarrow \infty$, agreeing with 2.1.

For the requested plot, put $[In]_0$ on the horizontal axis and I on the vertical axis. Draw a horizontal line at

$$I = \frac{k_c[Ac]_0}{\beta(k_b + k_c[Ac]_0)}.$$

It applies for positive $[In]_0$ over the range in which Ac remains effectively constant. At exactly $[In]_0 = 0$, the consumption ratio is undefined; its right-hand limit is the same height.

2.3

In scheme (4), the productive catalytic reaction regenerates In . A given amount of In can therefore mediate repeated consumption of Ac before being lost through reaction (4a).

For the usual first-order catalytic interpretation, write

$$v_{\text{loss}} = k_{\text{loss}}[A][In], \quad v_{\text{cat}} = k_{\text{cat}}[A][Ac][In].$$

Only the loss reaction consumes In , so

$$\frac{-d[Ac]/dt}{-d[In]/dt} = \frac{v_{\text{cat}}}{\beta v_{\text{loss}}} = \frac{k_{\text{cat}}[Ac]}{\beta k_{\text{loss}}}.$$

As the acceptor concentration increases without bound, productive reaction increasingly outcompetes inductor loss:

$$\lim_{[Ac]_0 \rightarrow \infty} I = \infty.$$

There is no stoichiometric ceiling of $1/\beta$ for this catalytic scheme.

2.4

The balanced reaction is



The species involved in this and the following part are:

Species	SMILES
Hydrogen molecule, H_2	[H][H]
Hydrogen bromide, HBr	[H]Br
Bromine molecule, Br_2	BrBr
Hydrogen atom, H	[H]
Bromine atom, Br	[Br]

The isolated hydrogen and bromine atoms are radicals.

For the elementary forward and reverse reactions,

$$r_5 = k_5[\text{Br}][\text{H}_2], \quad r_{-5} = k_{-5}[\text{HBr}][\text{H}].$$

Define the dimensionless reaction quotient

$$Q_5 = \frac{(p(\text{HBr})/p^\circ)(p(\text{H})/p^\circ)}{(p(\text{Br})/p^\circ)(p(\text{H}_2)/p^\circ)}.$$

Because the forward and reverse steps both involve two gas particles,

$$\frac{r_5}{r_{-5}} = \frac{K_5}{Q_5}, \quad K_5 = \exp\left(-\frac{\Delta G^\circ(5)}{RT}\right).$$

The specified pressures give $Q_5 = 1$. Using $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$,

$$\frac{r_5}{r_{-5}} = \exp\left[-\frac{66\,000 \text{ J mol}^{-1}}{(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(600 \text{ K})}\right] = 1.7947 \times 10^{-6}.$$

Thus

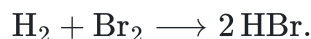
$$\frac{r_5}{r_{-5}} \approx 1.8 \times 10^{-6}.$$

2.5

The additional balanced step is



Adding reactions (5), in its forward direction, and (6) eliminates the radicals:



At steady state, production and consumption of hydrogen atoms balance:

$$\frac{d[\text{H}]}{dt} = r_5 - r_{-5} - r_6 = 0.$$

Therefore,

$$r_5 = r_{-5} + r_6.$$

Since $p(\text{Br}_2) = p(\text{HBr})$, their concentrations are equal at the same temperature. Consequently,

$$\frac{r_6}{r_{-5}} = \frac{k_6[\text{H}][\text{Br}_2]}{k_{-5}[\text{H}][\text{HBr}]} = \frac{k_6}{k_{-5}} = 10.$$

It follows that

$$\boxed{\frac{r_5}{r_{-5}} = 1 + 10 = 11.}$$

Using $r_5/r_{-5} = K_5/Q_5$, the steady-state quotient is

$$Q_5 = \frac{K_5}{11}.$$

The actual reaction Gibbs energy is therefore

$$\begin{aligned} \Delta G(5) &= \Delta G^\circ(5) + RT \ln Q_5 \\ &= \Delta G^\circ(5) + RT \ln K_5 - RT \ln 11 \\ &= -RT \ln 11. \end{aligned}$$

Numerically,

$$\Delta G(5) = -(8.314)(600) \ln 11 \text{ J mol}^{-1} = -11.9617 \text{ kJ mol}^{-1}.$$

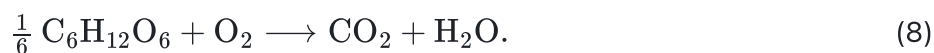
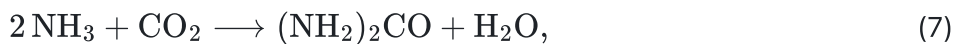
Hence

$$\boxed{\Delta G(5) = -12.0 \text{ kJ mol}^{-1}.}$$

Reaction (6) consumes hydrogen atoms and produces bromine atoms, lowering Q_5 . Thus reaction (5) has a negative **actual** Gibbs energy under the coupled conditions despite its positive **standard** Gibbs energy.

2.6

The balanced reactions, with the normalizations used in the question, are



Their molecular species are:

Species	SMILES
Ammonia, NH_3	N
Carbon dioxide, CO_2	O=C=O
Urea, $(\text{NH}_2)_2\text{CO}$	NC(=O)N
Water, H_2O	O
Dioxygen, O_2	O=O

Species	SMILES
Glucose, C ₆ H ₁₂ O ₆ , shown as open-chain D-glucose	<chem>O=C[C@H](O)[C@@H](O)[C@H](O)[C@H](O)CO</chem>

The glucose SMILES specifies the configuration of the open-chain D form, not a particular conformation or cyclic anomer. These distinctions do not enter the calculation using the supplied Gibbs energy.

For simultaneous reactions at constant temperature and pressure,

$$\frac{1}{V} \frac{dG_{\text{syst}}}{dt} = r_7 \Delta G(7) + r_8 \Delta G(8).$$

The stated requirement is

$$r_7 \Delta G(7) + r_8 \Delta G(8) < 0.$$

Substitution gives

$$r_7(46.0 \text{ kJ mol}^{-1}) < (6.0 \times 10^{-8} \text{ mol dm}^{-3} \text{ min}^{-1})(481.2 \text{ kJ mol}^{-1}).$$

Thus

$$r_7 < \frac{481.2}{46.0} (6.0 \times 10^{-8}) = 6.2765 \times 10^{-7} \text{ mol dm}^{-3} \text{ min}^{-1}.$$

The upper limiting rate, to the precision of the supplied rate, is

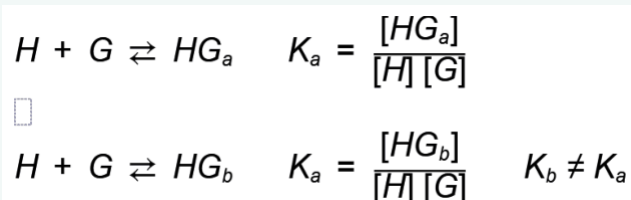
$$r_{7,\text{lim}} = 6.3 \times 10^{-7} \text{ mol dm}^{-3} \text{ min}^{-1}.$$

At the unrounded limiting value, the two Gibbs-energy contributions exactly cancel. Strict Gibbs-energy decrease requires a smaller rate. No additional factor of six is needed: both $r(8)$ and $\Delta G(8)$ refer to reaction (8) **as written**.

The solution was checked against the official solution. Where this solution differs from the official solution, the official solution contains an error or a misprint.

Problem 3: Two binding centers – competition or cooperation?

Many chemical reactions in living organisms include the formation of "host-guest" complexes where the host molecule reversibly binds one or several guest molecules. Consider a host molecule **H** with two binding centers – say, *a* and *b* which have different affinities for the guest molecules **G**:



where HG_a and HG_b denote a complex where guest is bound to *a* center and *b* center, respectively. K_a and K_b are the binding constants for the centers *a* and *b*, brackets denote molar concentrations.

Attachment of one G molecule to H can change the binding ability of the second centre. This change is described by the "interaction factor" β which reflects the influence of one binding center on another and is defined as follows:

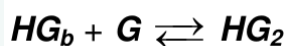
$$HG_a + G \rightleftharpoons HG_2$$

$$\frac{[HG_2]}{[HG_a][G]} = \beta K_b$$

where HG_2 is the completely bound complex.

3.1 Determine the range of values (or one value, if necessary) of β which correspond to three possible ways of interaction between binding centers: a) cooperation (binding by one center facilitates subsequent binding); b) competition (first binding complicates the second); c) independence (no interaction).

3.2 Find the equilibrium constant for the process:

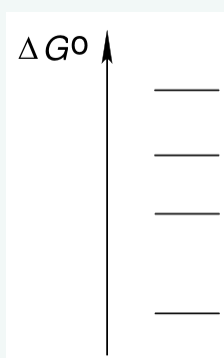


in terms of binding constant(s) and interaction factor.

3.3 The solution was prepared with the initial concentrations $[H]_0 = 1$ and $[G]_0 = 2$. After the reactions were completed, the concentration of H decreased by 10 times and that of G by 4 times. For these host and guest, $K_b = 2K_a$. Determine the concentrations of all other species in the solution and find the binding constant K_a and the factor β .

Note: If you could not answer this question, for further calculations use reference values $K_a = 3.14$ and $\beta = 2.72$.

3.4 Find the correct order of standard molar Gibbs energies of formation of host H and all host-guest complexes from H and G. In the scheme below, write the corresponding chemical formula near every line.



3.5 Some amount of G was added to 1 mole of H and the mixture was dissolved in water to obtain 1 liter of the solution. The number of the totally bound molecules HG_2 in the solution is equal to the total number of single-bound molecules HG. Find the initial amount of G (in mol). The constants K_a and K_b and the factor β are the same as in question 3.3.

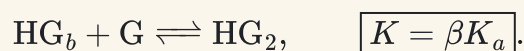
3.6 What would be the equilibrium composition of the solution if: a) $\beta = 0$; b) β is very large ($\beta \rightarrow \infty$). The constants K_a and K_b as well as the initial concentrations of H and G are the same as in question 2.1.

Official English text of the problem.

Answers

- **3.1** (a) Cooperation: $\beta > 1$. (b) Competition: $0 \leq \beta < 1$, with $\beta = 0$ representing complete exclusion of the second guest. (c) Independence: $\beta = 1$.

- **3.2**



- **3.3**

$$[\text{HG}_a] = 0.10, \quad [\text{HG}_b] = 0.20, \quad [\text{HG}_2] = 0.60 \quad (\text{mol L}^{-1})$$

$$K_a = 2 \text{ L mol}^{-1}, \quad K_b = 4 \text{ L mol}^{-1}, \quad \beta = 3.$$

- **3.4** Label the four lines **from top to bottom**:



- **3.5**

$$n_0(\text{G}) = \frac{11}{8} \text{ mol} = 1.375 \text{ mol} \approx 1.38 \text{ mol}.$$

- **3.6** Interpreting "question 2.1" as **question 3.3**, the equilibrium concentrations are:

Species	(a) $\beta = 0, \text{ mol L}^{-1}$	(b) $\beta \rightarrow \infty, \text{ mol L}^{-1}$
H	0.1287	0
G	1.1287	0
HG_a	0.2904	0
HG_b	0.5809	0
HG_2	0	1

Solution

The species are the free host H, free guest G, singly bound host–guest complexes HG_a and HG_b at sites a and b , and doubly bound host–guest complex HG_2 . These are abstract molecular labels: the problem supplies no molecular connectivity, so identifying SMILES cannot be assigned.

Write

$$h = [\text{H}], \quad g = [\text{G}], \quad x = [\text{HG}_a], \quad y = [\text{HG}_b], \quad z = [\text{HG}_2].$$

The binding equilibria give

$$x = K_a h g, \quad y = K_b h g,$$

and

$$z = \beta K_b x g = \beta K_a K_b h g^2.$$

Conservation of host and guest gives

$$\boxed{H_T = h + x + y + z}, \quad \boxed{G_T = g + x + y + 2z},$$

where $H_T = [H]_0$ and $G_T = [G]_0$. The factor 2 counts the two guest molecules in each HG_2 .

3.1

For binding at site b , the two relevant reactions are



and



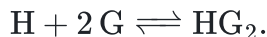
Thus β compares the affinity of site b when site a is occupied with its affinity when site a is empty:

- **Cooperation:** $\beta K_b > K_b$, hence $\beta > 1$.
- **Competition:** $\beta K_b < K_b$, hence $0 \leq \beta < 1$.
- **Independence:** $\beta K_b = K_b$, hence $\beta = 1$.

Ordinary finite equilibrium constants are positive. The value $\beta = 0$, explicitly considered in 3.6, is the limiting case in which double binding is completely prohibited.

3.2

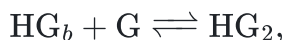
Both binding sequences lead to the same overall reaction:



Its overall concentration-based equilibrium constant is

$$\frac{z}{hg^2} = K_a(\beta K_b) = \beta K_a K_b.$$

For the requested reaction,



the equilibrium constant is therefore

$$K = \frac{z}{yg} = \frac{\beta K_a K_b h g^2}{K_b h g^2} = \boxed{\beta K_a}.$$

This also shows that the same interaction factor applies whichever site binds first.

3.3

The free equilibrium concentrations are

$$h = \frac{1}{10} = 0.10 \text{ mol L}^{-1}, \quad g = \frac{2}{4} = 0.50 \text{ mol L}^{-1}.$$

The host balance gives

$$x + y + z = 1 - 0.10 = 0.90 \text{ mol L}^{-1},$$

and the guest balance gives

$$x + y + 2z = 2 - 0.50 = 1.50 \text{ mol L}^{-1}.$$

Subtracting,

$$z = 0.60 \text{ mol L}^{-1}, \quad x + y = 0.30 \text{ mol L}^{-1}.$$

Because

$$\frac{y}{x} = \frac{K_b}{K_a} = 2,$$

we obtain

$$\boxed{x = 0.10 \text{ mol L}^{-1}}, \quad \boxed{y = 0.20 \text{ mol L}^{-1}}.$$

Consequently,

$$K_a = \frac{x}{hg} = \frac{0.10}{(0.10)(0.50)} = \boxed{2 \text{ L mol}^{-1}},$$

and

$$K_b = 2K_a = \boxed{4 \text{ L mol}^{-1}}.$$

Finally,

$$\beta = \frac{z}{K_b x g} = \frac{0.60}{4(0.10)(0.50)} = \boxed{3}.$$

The interaction is therefore cooperative.

3.4

The energies requested are formation energies **from the unbound host and guest**. Take the unbound host as the zero reference.

For a reaction,

$$\Delta_r G^\circ = -RT \ln K^\circ.$$

Here K° must be dimensionless. With the standard concentration

$$c^\circ = 1 \text{ mol L}^{-1},$$

the dimensionless association constants are $K_a c^\circ = 2$, $K_b c^\circ = 4$, and

$$\beta K_a K_b (c^\circ)^2 = 24.$$

Host species	Formation reaction from free host and guest	Relative standard formation energy
H	Reference state	0
HG _a	$\text{H} + \text{G} \rightleftharpoons \text{HG}_a$	$-RT \ln 2$
HG _b	$\text{H} + \text{G} \rightleftharpoons \text{HG}_b$	$-RT \ln 4$
HG ₂	$\text{H} + 2 \text{G} \rightleftharpoons \text{HG}_2$	$-RT \ln 24$

Since

$$0 > -\ln 2 > -\ln 4 > -\ln 24,$$

the order from highest to lowest energy is

$$\boxed{\text{H} > \text{HG}_a > \text{HG}_b > \text{HG}_2}.$$

Accordingly, write H beside the top line, HG_a beside the second, HG_b beside the third, and HG_2 beside the bottom line. Equivalently, with a common total composition, the compared states are $H + 2G$, $HG_a + G$, $HG_b + G$, and HG_2 .

3.5

The total host concentration is

$$H_T = \frac{1 \text{ mol}}{1 \text{ L}} = 1 \text{ mol L}^{-1}.$$

The stated condition is

$$z = x + y.$$

Using the equilibrium expressions,

$$\beta K_a K_b h g^2 = (K_a + K_b) h g.$$

For a positive amount of added guest, $g > 0$, so

$$g = \frac{K_a + K_b}{\beta K_a K_b} = \frac{6 \text{ L mol}^{-1}}{24 \text{ L}^2 \text{ mol}^{-2}} = \boxed{0.25 \text{ mol L}^{-1}}.$$

The host balance becomes

$$H_T = h [1 + (K_a + K_b)g + \beta K_a K_b g^2],$$

hence

$$h = \frac{1}{1 + 6(0.25) + 24(0.25)^2} = 0.25 \text{ mol L}^{-1}.$$

The complex concentrations are

$$x = 2(0.25)(0.25) = 0.125 \text{ mol L}^{-1},$$

$$y = 4(0.25)(0.25) = 0.250 \text{ mol L}^{-1},$$

$$z = x + y = 0.375 \text{ mol L}^{-1}.$$

The initial guest amount must include both free and bound guest:

$$\begin{aligned} n_0(G) &= V(g + x + y + 2z) \\ &= (1 \text{ L})(0.25 + 0.125 + 0.250 + 2 \times 0.375) \text{ mol L}^{-1} \\ &= \boxed{1.375 \text{ mol} \approx 1.38 \text{ mol}}. \end{aligned}$$

3.6

Here the reference to "question 2.1" is interpreted as referring to 3.3:

$$\begin{aligned} H_T &= 1 \text{ mol L}^{-1}, & G_T &= 2 \text{ mol L}^{-1}, \\ K_a &= 2 \text{ L mol}^{-1}, & K_b &= 4 \text{ L mol}^{-1}. \end{aligned}$$

(a) $\beta = 0$

Double binding is excluded:

$$z = 0.$$

Subtracting the host balance from the guest balance gives

$$g - h = 1 \text{ mol L}^{-1}.$$

Also,

$$x + y = (K_a + K_b)hg.$$

Thus

$$h + (6 \text{ L mol}^{-1})h (h + 1 \text{ mol L}^{-1}) = 1 \text{ mol L}^{-1}.$$

With $u = h/c^\circ$, this becomes

$$6u^2 + 7u - 1 = 0.$$

Only the positive root is physical:

$$h = \frac{\sqrt{73} - 7}{12} \text{ mol L}^{-1} \approx \boxed{0.1287 \text{ mol L}^{-1}}.$$

Therefore,

$$g = h + 1 \text{ mol L}^{-1} \approx \boxed{1.1287 \text{ mol L}^{-1}}.$$

Since $y = 2x$ and $x + y = H_T - h$,

$$x = \frac{H_T - h}{3} \approx \boxed{0.2904 \text{ mol L}^{-1}},$$

$$y = \frac{2(H_T - h)}{3} \approx \boxed{0.5809 \text{ mol L}^{-1}}, \quad \boxed{z = 0}.$$

(b) $\beta \rightarrow \infty$

Because $G_T = 2H_T$, subtracting twice the host balance from the guest balance yields

$$g = 2h + x + y.$$

Using $x + y = (K_a + K_b)hg$,

$$h = \frac{g}{2 + (K_a + K_b)g}.$$

Consequently,

$$z = \beta K_a K_b h g^2 = \frac{\beta K_a K_b g^3}{2 + (K_a + K_b)g}.$$

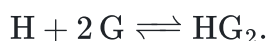
The concentration z cannot exceed H_T . As $\beta \rightarrow \infty$, the last expression therefore requires $g \rightarrow 0$. It follows that

$$h \rightarrow 0, \quad x = K_a h g \rightarrow 0, \quad y = K_b h g \rightarrow 0.$$

The host balance then gives

$$\boxed{z \rightarrow H_T = 1 \text{ mol L}^{-1}}.$$

Thus all host approaches the doubly bound form, consuming the entire available guest supply in the overall reaction



The solution was checked against the official solution.

Problem 4: From one yellow powder to another: A simple inorganic riddle

The yellow binary compound X_1 was completely dissolved in concentrated nitric acid by heating, the gas evolved is 1.586 times denser than air. Upon adding an excess of barium chloride to the solution formed a white solid X_2 precipitates. It was filtered. The filtrate reacts with an excess of silver sulfate solution forming a precipitate of two solids X_2 and X_3 , also separated from solution by filtration. To the new filtrate the solution of sodium hydroxide was being added drop-wise until the solution became nearly neutral (about pH 7). At this time a yellow powder X_4 (77.31 wt.% of Ag) crystallized from the solution. The mass of X_4 is nearly 2.4 times larger than that the mass of the first portion of X_2 .

4.1 Determine the chemical formulae of $X_1 - X_4$.

4.2 Determine the chemical formula of the gas and provide equations for all reactions in ionic or non-ionic form.

4.3 In the structural unit of X_1 all atoms of only one element are in equivalent positions. Draw the structure of X_1 .

4.4 Predict the products of X_1 interaction with:

- excess oxygen;
- excess of hot concentrated sulfuric acid;
- solid KClO_3 with grinding.

Write down the equations of the reactions.

Official English text of the problem.

Answers

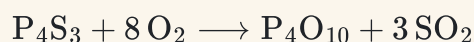
• 4.1

Compound	Formula	Name	SMILES
X_1	P_4S_3	Tetraphosphorus trisulfide, also called phosphorus sesquisulfide	<chem>P12P3P1SP(S2)S3</chem>
X_2	BaSO_4	Barium sulfate	<chem>[Ba+2].[O-]S(=O)(=O)[O-]</chem>
X_3	AgCl	Silver(I) chloride	<chem>[Ag+].[Cl-]</chem>
X_4	Ag_3PO_4	Silver(I) phosphate	<chem>[Ag+].[Ag+].[Ag+].[O-]P(=O)([O-])[O-]</chem>

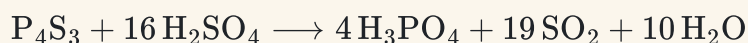
- 4.2** The gas is **nitrogen dioxide**, NO_2 , SMILES [O-][N+]=O. The balanced reaction equations are given below.

- **4.3** The P_4S_3 molecule has a triangular base of three directly bonded phosphorus atoms. Each basal phosphorus is connected through one sulfur atom to a fourth, apical phosphorus. All three sulfur atoms are equivalent; the phosphorus atoms occupy two distinct environments.

- **4.4(a)**



- **4.4(b)**



- **4.4(c)**



The disconnected SMILES for salts specify their constituent ions, rather than their crystal structures.

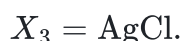
Solution

4.1 — Identification of X_1 – X_4

The first white precipitate is consistent with **barium sulfate**, formed from sulfate produced during oxidation of sulfur in X_1 . Its precipitation from the strongly acidic solution supports this identification:



The added barium chloride also introduces chloride ions. Subsequent addition of silver sulfate precipitates the remaining barium as more barium sulfate, while silver ions precipitate chloride as **silver(I) chloride**:



The final yellow precipitate is **silver(I) phosphate**. Using standard atomic molar masses,

$$M(\text{Ag}_3\text{PO}_4) = 3(107.868) + 30.974 + 4(15.999) = 418.57 \text{ g mol}^{-1}.$$

Its calculated silver content is

$$w(\text{Ag}) = \frac{3(107.868)}{418.57} \times 100\% = 77.31\%,$$

matching the stated value. Therefore,



The binary starting material consequently contains phosphorus and sulfur. Each mole of phosphorus atoms gives one mole of silver phosphate, while each mole of sulfur atoms gives one mole of barium sulfate in the **first** precipitation.

With

$$M(\text{BaSO}_4) = 233.38 \text{ g mol}^{-1},$$

the mass ratio gives

$$\frac{m(X_4)}{m(X_2, \text{ first portion})} = \frac{n(\text{P}) M(\text{Ag}_3\text{PO}_4)}{n(\text{S}) M(\text{BaSO}_4)} \approx 2.4.$$

Thus,

$$\frac{n(\text{P})}{n(\text{S})} \approx 2.4 \frac{233.38}{418.57} = 1.338 \approx \frac{4}{3}.$$

The starting compound is therefore



As a check, its predicted precipitate mass ratio is

$$\frac{4M(\text{Ag}_3\text{PO}_4)}{3M(\text{BaSO}_4)} = \frac{4(418.57)}{3(233.38)} = 2.391,$$

consistent with “nearly 2.4.”

Only the first portion of barium sulfate is used here: sulfate in the second portion comes from the added silver sulfate.

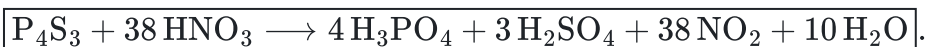
4.2 — Gas identification and reaction equations

At the same temperature and pressure, gas density is proportional to molar mass. Taking the mean molar mass of air as approximately 29.0 g mol^{-1} ,

$$M_{\text{gas}} = 1.586(29.0) = 46.0 \text{ g mol}^{-1}.$$

This identifies **nitrogen dioxide**, NO_2 , whose molar mass is approximately 46.0 g mol^{-1} . Its SMILES is [O-][N+]=O; it is a bent, odd-electron molecule.

Oxidative dissolution. Hot concentrated nitric acid oxidizes phosphorus to phosphoric acid and sulfur to sulfuric acid:

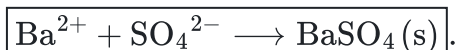


The molecular species used here are:

Name	Formula	SMILES
Nitric acid	HNO_3	<chem>O=[N+]([O-])O</chem>
Phosphoric acid	H_3PO_4	<chem>OP(=O)(O)O</chem>
Sulfuric acid	H_2SO_4	<chem>OS(=O)(=O)O</chem>
Water	H_2O	<chem>O</chem>

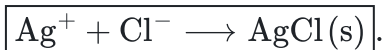
For the electron balance, the three sulfur atoms initially have oxidation state -2 , so the total oxidation-state sum for phosphorus is $+6$. Oxidation of the four phosphorus atoms to $+5$ releases $20 - 6 = 14$ electrons. Oxidation of three sulfur atoms from -2 to $+6$ releases 24 electrons. The total is 38, matching reduction of 38 nitrogen atoms from $+5$ to $+4$.

First precipitation. Barium chloride, SMILES [Ba+2].[Cl-].[Cl-], supplies barium ions, [Ba+2], which precipitate sulfate ions, [O-]S(=O)(=O)[O-]:



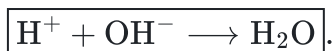
Phosphoric acid remains dissolved under these acidic conditions.

Second precipitation. Silver(I) sulfate, SMILES [Ag+].[Ag+].[O-]S(=O)(=O)[O-], supplies sulfate ions that remove the excess barium by the same barium sulfate precipitation reaction. Its silver(I) ions, [Ag+], also remove chloride ions, [Cl-]:

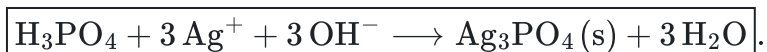


Thus, the second precipitate contains both BaSO_4 and AgCl . Excess silver ions remain in the filtrate.

Neutralization and yellow precipitation. Sodium hydroxide, SMILES $[\text{Na}^+] \cdot [\text{OH}^-]$, supplies hydroxide ions, $[\text{OH}^-]$, which neutralize hydrogen ions, $[\text{H}^+]$:



As the acidity decreases, silver phosphate precipitates. A net ionic equation incorporating phosphate deprotonation is



This equation does not require fully deprotonated phosphate to be the predominant dissolved phosphate species at pH 7: precipitation draws the acid–base equilibria toward further deprotonation.

4.3 — Structure of X_1

Tetraphosphorus trisulfide, P_4S_3 , SMILES P12P3P1SP(S2)S3 , has a cage structure.

To draw it precisely:

1. Draw three phosphorus atoms at the vertices of a triangular base, with a single phosphorus–phosphorus bond along each side.
2. Place a fourth phosphorus atom above the centre of this triangle.
3. Connect the apical phosphorus to each basal phosphorus through a separate sulfur atom, giving three bent $\text{P}–\text{S}–\text{P}$ bridges.
4. Draw all bonds as single bonds. Each phosphorus has one lone pair, and each sulfur has two lone pairs.

There are three direct phosphorus–phosphorus bonds and six phosphorus–sulfur bonds, with no sulfur–sulfur bonds.

The molecular symmetry is C_{3v} . The three sulfur atoms are equivalent, as are the three basal phosphorus atoms. The apical phosphorus is distinct: it bonds to three sulfur atoms, whereas each basal phosphorus bonds to two phosphorus atoms and one sulfur atom. This satisfies the stated equivalence condition.

4.4 — Reactions of X_1

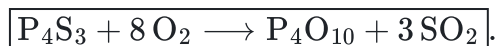
The additional species appearing in these reactions are:

Name	Formula	SMILES
Dioxygen	O_2	$\text{O}=\text{O}$
Tetraphosphorus decaoxide, phosphorus(V) oxide	P_4O_{10}	$\text{O}=\text{P12OP3(=O)OP(=O)(O1)OP(=O)(O2)O3}$
Sulfur dioxide	SO_2	$\text{O}=\text{S}=\text{O}$
Potassium chlorate	KClO_3	$[\text{K}^+] \cdot [\text{O}^-]\text{Cl}(=\text{O})=\text{O}$
Potassium chloride	KCl	$[\text{K}^+] \cdot [\text{Cl}^-]$

The molecular P_4O_{10} cage has four phosphorus atoms arranged tetrahedrally, six bridging oxygen atoms—one along each tetrahedral edge—and one terminal oxygen at each phosphorus. The conventional dioxygen SMILES records connectivity; ground-state dioxygen is a triplet.

(a) Excess oxygen

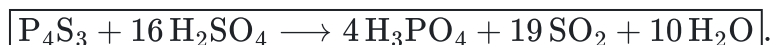
Combustion gives phosphorus(V) oxide and sulfur dioxide:



Phosphorus reaches oxidation state +5, while sulfur reaches +4.

(b) Excess hot concentrated sulfuric acid

Sulfuric acid acts as the oxidant and is reduced to sulfur dioxide. The phosphorus becomes phosphoric acid, and the sulfur originally present in P_4S_3 also becomes sulfur dioxide:



The phosphorus atoms release 14 electrons in total, and the three sulfur atoms release

$$3[4 - (-2)] = 18$$

electrons. Thus, 32 electrons are released. Each sulfuric-acid sulfur atom accepts two electrons on changing from +6 to +4, requiring 16 sulfuric acid molecules. The 19 sulfur dioxide molecules contain 16 sulfur atoms from the acid and three from the starting compound.

(c) Solid potassium chlorate with grinding

Chlorate oxidizes the phosphorus and sulfur to phosphorus(V) oxide and sulfur dioxide, while chlorine is reduced from +5 to −1:



Each P_4S_3 molecule releases 32 electrons, and each chlorate accepts six. The smallest matching totals are

$$3(32) = 16(6) = 96,$$

giving the coefficients shown.

The solution was checked against the official solution.

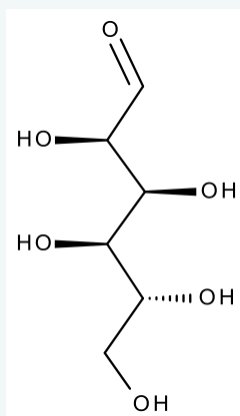
Problem 5: Indispensable glucose

Carbohydrates are the most important providers of energy for living cells. Monosaccharide glucose is a source of energy for the living cell, but for persons who suffer from diabetes glucose may be dangerous. High level of glucose may lead to cardiovascular diseases and even death. That is why people avoid consuming too much carbohydrates and glucose particularly.

A. Determination of reducing sugars in fruit juice

One of the technique for determination of reducing sugars in different samples includes the use of Fehling's reagent. A 10.00 cm^3 aliquot of fruit juice (assuming the initial sample contained only glucose and fructose) was transferred into a titration flask and Fehling's reagent was added. This

reagent was prepared by mixing 50.00 cm^3 of copper sulfate solution, $c = 0.04000 \text{ mol dm}^{-3}$ (solution A) and potassium-sodium tartrate and sodium hydroxide (solution B). Solution C thus obtained, was then heated and red precipitate was formed.



Glucose

5.1 Write the balanced ionic equation of chemical reaction occurring upon heating of the solution C. Use Cu^{2+} for initial copper solution.

After that 10 cm^3 of 10% solution of potassium iodide and sulfuric acid solution ($c = 1 \text{ mol dm}^{-3}$) were added to the flask. The mixture was covered with watch glass and was then placed in a dark place. An excess of iodine was then titrated with sodium thiosulphate solution ($c = 0.05078 \text{ mol dm}^{-3}$). A volume of 11.87 cm^3 of the titrant was required to reach the endpoint.

5.2 Write the balanced equation(s) in molecular or ionic form for all the reactions taking place in the flask.

5.3 Consider that all fructose was transformed into glucose under the experimental conditions. Calculate the total mass concentration of sugars (in g dm^{-3}) in a fruit juice.

$$M = 180.16 \text{ g mol}^{-1}.$$

A new 10.00 cm^3 aliquot of the same juice was treated with a 10.00 cm^3 portion of acidified potassium iodate(V) solution ($0.01502 \text{ mol dm}^{-3}$) and 10 cm^3 of 10 % solution of potassium iodide. After the mixture turned brown, an excess of sodium hydroxide solution was added. The flask was then covered with a watch glass and put into a dark place. The obtained solution was acidified and titrated with a solution of sodium thiosulphate ($c = 0.01089 \text{ mol dm}^{-3}$). The average titrant volume used for titration was 23.43 cm^3 . Note that fructose is not converted into glucose under these conditions.

5.4 Write all the balanced equations for the described reactions in molecular or ionic form.

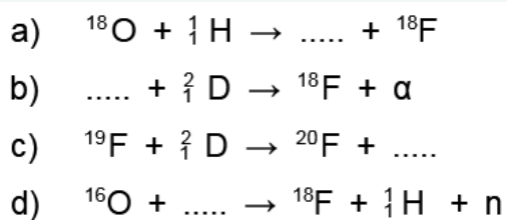
5.5 Calculate the mass concentration of each sugar (in g dm^{-3}) in the juice.

5.6 One bread exchange unit (1 BEU) corresponds to the content of 12 g of digestible carbohydrates in a product. How many BEU are in one glass (200 cm^3) of juice?

B. Diagnosis of diseases

The derivative of glucose, 2-deoxy-2-(^{18}F)fluoro-D-glucose (FDG), is the most common radiopharmaceutical for diagnosis of cancer using positron emission tomography. The first step of FDG preparation is to produce a radionuclide fluoro-18 by nuclear reaction in a cyclotron. The next step is the radiochemical synthesis. Fluorine-18 is introduced into D-glucose molecule by nucleophilic substitution. 2-deoxy-2-(^{18}F)fluoro-D-glucose once injected into the patient actively accumulates in cells of malignant tumors; this process is accompanied by decomposition of fluorine-18. This radionuclide is a β^+ emitter – nucleus emits a positron (anti-electron). Positron interacts with an electron and after that annihilation occurs, which can be detected. This allows determining precisely the tumor sizes and type.

5.7 Complete the nuclear reactions leading to various fluorine isotopes.



5.8 The decay mode of unstable light nuclei depends on the ratio between the number of neutrons and protons in them. If this ratio is greater than that for a stable isotope then the nucleus decays in a β^- -mode, if it is smaller – in a β^+ -mode.

Determine the type of decay for the nuclei in the table:

Nucleus	^{11}C	^{20}F	^{17}F	^{14}C
Decay mode				

When nuclear reaction (a) is used for fluorine-18 preparation, the target material is presented as water enriched with $\text{H}_2\ ^{18}\text{O}$. The presence of usual water $\text{H}_2\ ^{16}\text{O}$ leads to a side nuclear reaction with ^{16}O , leading to the formation of isotope ^{17}F .

5.9 It is known that within five minutes after completion of irradiation of the target the ratio of radioactivities of ^{18}F and ^{17}F is $1 \cdot 10^5$. Assuming that irradiation time is short, the radioactivity of each isotope is proportional to the nuclear reaction yield and the mole fraction of a component in the irradiated target, calculate the mass fraction of $\text{H}_2\ ^{18}\text{O}$ in the target. $t_{1/2}(^{18}\text{F}) = 109.7$ minutes, $t_{1/2}(^{17}\text{F}) = 65$ seconds. The ratio between nuclear reactions yields is

$$\eta_{^{18}\text{O} \rightarrow ^{18}\text{F}} / \eta_{^{16}\text{O} \rightarrow ^{17}\text{F}} = 144.7.$$

5.10 Calculate the yield of labeling D-glucose with fluorine-18, if initial radioactivity of a fluorine-18 sample was 600.0 MBq and radioactivity of the obtained 2-deoxy-2-(^{18}F)fluoro-D-glucose is 528.2 MBq. Synthesis time is 3.5 minutes.

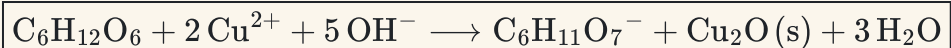
5.11 Biological half-life (through the excretory organs) of 2-deoxy-2-(^{18}F)fluoro-D-glucose is 120.0 minutes. How much radioactivity (in MBq) will remain in the patient ten hours after injection of FDG with the initial radioactivity of 450.0 MBq.

Official English text of the problem.

Answers

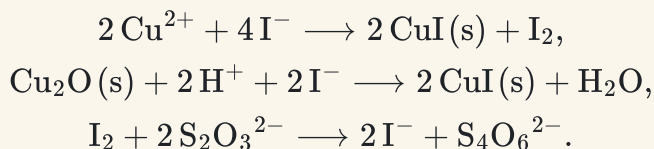
Names and SMILES for the chemical species appearing below are collected at the beginning of the Solution.

- 5.1



Glucose is oxidized to D-gluconate; the red precipitate is copper(I) oxide.

- 5.2 The principal reactions are

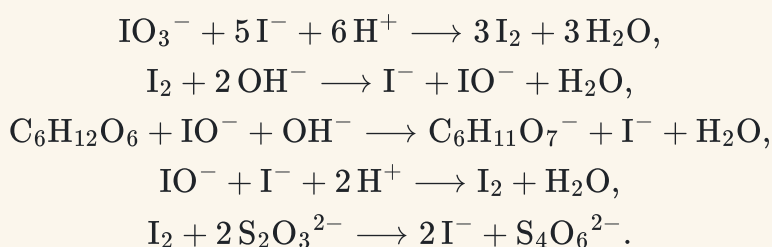


Acid–base reactions and iodine speciation are included in the detailed solution.

- 5.3

$$\rho_{\text{total}} = 12.59 \text{ g dm}^{-3}$$

- 5.4 The analytical reaction sequence is



Possible hypiodite disproportionation and the acid–base reactions are given below.

- 5.5

$$\rho_{\text{glucose}} = 5.820 \text{ g dm}^{-3}$$

$$\rho_{\text{fructose}} = 6.767 \text{ g dm}^{-3}$$

- 5.6

$$0.210 \text{ BEU per } 200 \text{ cm}^3 \text{ glass}$$

- 5.7 Missing particles or nuclei:

- (a) neutron, ${}_0^1\text{n}$;
- (b) neon-20, ${}_{10}^{20}\text{Ne}$;
- (c) proton, ${}_1^1\text{H}$;
- (d) alpha particle, ${}_2^4\text{He}$.

- 5.8

Nucleus	${}^{11}\text{C}$	${}^{20}\text{F}$	${}^{17}\text{F}$	${}^{14}\text{C}$
Decay mode	β^+	β^-	β^+	β^-

- **5.9** Including the decay-constant ratio when converting nuclear-production yields into activities,

$$w(\text{H}_2^{18}\text{O}) \approx 0.999695 \approx 99.97\%$$

- **5.10**

$$\text{Decay-corrected labeling yield} = 90.0\%$$

- **5.11**

$$A(10 \text{ h}) \approx 0.317 \text{ MBq}$$

Solution

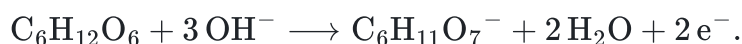
The following identities and SMILES apply throughout. The carbohydrate SMILES describe **open-chain forms**, with the stereochemistry retained from D-glucose. They do not specify the populations or conformations of cyclic forms in solution.

Name	Formula	SMILES
D-Glucose	$\text{C}_6\text{H}_{12}\text{O}_6$	<chem>O=C[C@H](O)[C@@H](O)[C@H](O)[C@H](O)CO</chem>
D-Fructose	$\text{C}_6\text{H}_{12}\text{O}_6$	<chem>OCC(=O)[C@@H](O)[C@H](O)[C@H](O)CO</chem>
D-Gluconate	$\text{C}_6\text{H}_{11}\text{O}_7^-$	<chem>O=C([O-])[C@H](O)[C@@H](O)[C@H](O)[C@H](O)CO</chem>
D-Gluconic acid	$\text{C}_6\text{H}_{12}\text{O}_7$	<chem>O=C(O)[C@H](O)[C@@H](O)[C@H](O)[C@H](O)CO</chem>
2-Deoxy-2-(fluorine-18)fluoro-D-glucose, FDG	$\text{C}_6\text{H}_{11}^{18}\text{FO}_5$	<chem>O=C[C@H]([18F])[C@@H](O)[C@H](O)[C@H](O)CO</chem>
Water	H_2O	<chem>O</chem>
Oxygen-18 water	H_2^{18}O	<chem>[18OH2]</chem>
Oxygen-16 water	H_2^{16}O	<chem>[16OH2]</chem>
Copper(II) ion	Cu^{2+}	<chem>[Cu+2]</chem>
Copper(I) oxide	Cu_2O	<chem>[Cu+] . [Cu+] . [O-2]</chem>
Copper(I) iodide	CuI	<chem>[Cu+] . [I-]</chem>
Hydrogen ion, aqueous proton	H^+	<chem>[H+]</chem>
Hydroxide ion	OH^-	<chem>[OH-]</chem>
Iodide ion	I^-	<chem>[I-]</chem>
Iodine	I_2	<chem>II</chem>
Triiodide ion	I_3^-	<chem>I [I-] I</chem>
Iodate(V) ion	IO_3^-	<chem>[O-]I(=O)=O</chem>
Hypoiodite ion	IO^-	<chem>[O-]I</chem>
Thiosulfate ion	$\text{S}_2\text{O}_3^{2-}$	<chem>[O-]S(=O)(=O)[S-]</chem>
Tetrathionate ion	$\text{S}_4\text{O}_6^{2-}$	<chem>[O-]S(=O)(=O)SSS(=O)(=O)[O-]</chem>

The copper(I) compounds are extended solids: their dot-separated SMILES give ionic formula units, not crystal structures. Triiodide is approximately linear; its SMILES does not encode that geometry or its delocalized bonding. Nuclear notation below describes nuclei and elementary particles, for which molecular SMILES are not applicable.

5.1 — Reaction with Fehling's reagent

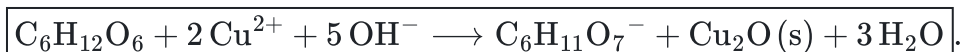
The aldehyde group of open-chain glucose is oxidized to a carboxylate group, releasing two electrons:



Two copper(II) ions each accept one electron, forming copper(I) oxide:



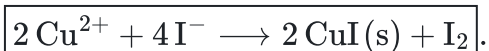
Adding the half-reactions gives



Thus, **one mole of glucose consumes two moles of copper(II)**. Under the stated experimental assumption, fructose is converted into glucose and contributes the same reducing capacity.

5.2 — Addition of acid and iodide, followed by titration

Residual copper(II) oxidizes iodide to iodine. The copper(I) produced precipitates as copper(I) iodide:

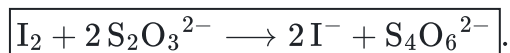


The copper(I) oxide already formed also becomes copper(I) iodide:

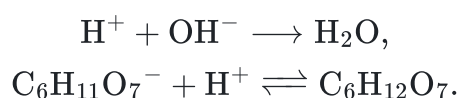


This second reaction produces **no iodine**, because copper remains in oxidation state +1.

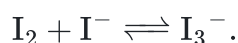
Iodine is titrated with thiosulfate, producing tetrathionate:



Acid addition also neutralizes hydroxide and protonates gluconate:



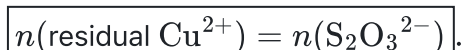
In excess iodide, iodine participates in the equilibrium



The equivalent titration equation is then



Either iodine representation gives the same analytical relationship:



5.3 — Total mass concentration of sugars

The initial amount of copper(II) is

$$n_{\text{Cu},0} = (0.04000 \text{ mol dm}^{-3})(0.05000 \text{ dm}^3) = 2.000 \times 10^{-3} \text{ mol}.$$

The amount of thiosulfate used is

$$n_{\text{thio}} = (0.05078)(0.01187) = 6.027586 \times 10^{-4} \text{ mol.}$$

This equals the residual amount of copper(II). Therefore, using the two-to-one copper-to-sugar stoichiometry,

$$\begin{aligned} n_{\text{glucose}} + n_{\text{fructose}} &= \frac{n_{\text{Cu},0} - n_{\text{thio}}}{2} \\ &= \frac{2.000 \times 10^{-3} - 6.027586 \times 10^{-4}}{2} \\ &= 6.986207 \times 10^{-4} \text{ mol.} \end{aligned}$$

Both sugars have the given molar mass. The total mass concentration is

$$\begin{aligned} \rho_{\text{total}} &= \frac{(6.986207 \times 10^{-4} \text{ mol})(180.16 \text{ g mol}^{-1})}{0.01000 \text{ dm}^3} \\ &= 12.58635 \text{ g dm}^{-3}. \end{aligned}$$

$$\boxed{\rho_{\text{total}} = 12.59 \text{ g dm}^{-3}}$$

5.4 — Selective determination of glucose

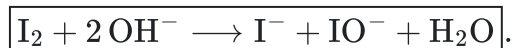
Acidified iodate oxidizes iodide, generating iodine:



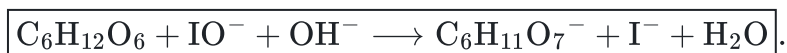
Addition of excess hydroxide neutralizes the acid,



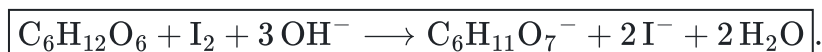
and converts iodine into iodide and hypoiodite:



Hypoiodite oxidizes glucose to gluconate:



Combining the last two oxidation-related equations gives



Consequently, **one mole of glucose consumes one mole of iodine**. Fructose has a ketone group and, under the explicitly stated conditions, does not isomerize into glucose; it therefore does not contribute to this determination.

After the reaction, acidification regenerates iodine from unused hypoiodite:



Hypoiodite can also disproportionate:

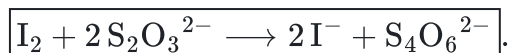


Any iodate formed by this process regenerates iodine upon acidification through the first equation of this part. Thus, this redistribution does not change the number of remaining oxidizing equivalents.

Acidification also neutralizes remaining hydroxide and protonates gluconate:



Finally, the regenerated iodine is titrated:



The triiodide equilibrium described in 5.2 also applies.

5.5 — Concentrations of glucose and fructose

Initially,

$$n(\text{IO}_3^-) = (0.01502 \text{ mol dm}^{-3})(0.01000 \text{ dm}^3) = 1.502 \times 10^{-4} \text{ mol}.$$

Each mole of iodate generates three moles of iodine:

$$n_{\text{I}_2,0} = 3(1.502 \times 10^{-4}) = 4.506 \times 10^{-4} \text{ mol}.$$

The second titration consumes

$$n_{\text{thio},2} = (0.01089)(0.02343) = 2.551527 \times 10^{-4} \text{ mol}.$$

Hence the remaining iodine equivalent is

$$n_{\text{I}_2,\text{remaining}} = \frac{n_{\text{thio},2}}{2} = 1.2757635 \times 10^{-4} \text{ mol}.$$

The difference gives the amount of glucose in the aliquot:

$$\begin{aligned} n_{\text{glucose}} &= 4.506 \times 10^{-4} - 1.2757635 \times 10^{-4} \\ &= 3.2302365 \times 10^{-4} \text{ mol}. \end{aligned}$$

Therefore,

$$\rho_{\text{glucose}} = \frac{(3.2302365 \times 10^{-4})(180.16)}{0.01000} = 5.819594 \text{ g dm}^{-3},$$

so

$$\boxed{\rho_{\text{glucose}} = 5.820 \text{ g dm}^{-3}}.$$

Using the unrounded total from 5.3,

$$\rho_{\text{fructose}} = 12.5863505 - 5.8195941 = 6.7667564 \text{ g dm}^{-3},$$

and hence

$$\boxed{\rho_{\text{fructose}} = 6.767 \text{ g dm}^{-3}}.$$

5.6 — Bread exchange units

The sugar mass in one glass is

$$m = (12.58635 \text{ g dm}^{-3})(0.200 \text{ dm}^3) = 2.51727 \text{ g}.$$

Thus,

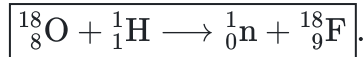
$$N_{\text{BEU}} = \frac{2.51727 \text{ g}}{12 \text{ g BEU}^{-1}} = 0.209773 \text{ BEU}.$$

$$\boxed{N_{\text{BEU}} \approx 0.210 \text{ BEU}}$$

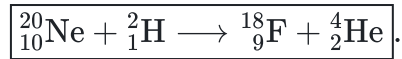
5.7 — Nuclear reactions

Both mass number A and atomic number Z must be conserved. The deuteron written as ${}^2_1\text{D}$ in the figure is written below as ${}^2_1\text{H}$.

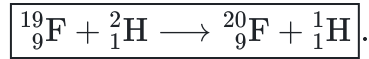
(a) The missing particle has $A = 18 + 1 - 18 = 1$ and $Z = 8 + 1 - 9 = 0$, identifying a neutron:



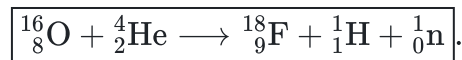
(b) The missing target nucleus has $A = 18 + 4 - 2 = 20$ and $Z = 9 + 2 - 1 = 10$, identifying neon-20:



(c) The missing particle has $A = 19 + 2 - 20 = 1$ and $Z = 9 + 1 - 9 = 1$, identifying a proton:



(d) The missing projectile has $A = 18 + 1 + 1 - 16 = 4$ and $Z = 9 + 1 - 8 = 2$, identifying an alpha particle:



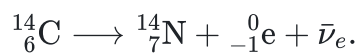
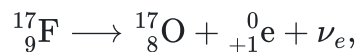
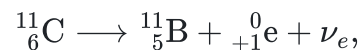
5.8 — Decay modes

A neutron-rich nucleus can lower its neutron-to-proton ratio by β^- decay, which converts a neutron into a proton. A proton-rich nucleus can increase that ratio by β^+ decay, which converts a proton into a neutron.

Stable carbon isotopes include ${}^{12}\text{C}$ and ${}^{13}\text{C}$, with neutron-to-proton ratios 1 and 7/6. Stable fluorine is ${}^{19}\text{F}$, with ratio 10/9.

Nucleus	Z	N	N/Z	Comparison with stable isotope(s)	Decay
${}^{11}\text{C}$	6	5	5/6	Proton-rich	β^+
${}^{20}\text{F}$	9	11	11/9	Neutron-rich	β^-
${}^{17}\text{F}$	9	8	8/9	Proton-rich	β^+
${}^{14}\text{C}$	6	8	8/6	Neutron-rich	β^-

The corresponding nuclear equations, including electron neutrinos or antineutrinos, are



5.9 — Mass fraction of oxygen-18 water

Let

$$r = \frac{n(\text{H}_2{}^{18}\text{O})}{n(\text{H}_2{}^{16}\text{O})}.$$

For short irradiation, taking the quoted reaction yields to describe **numbers of nuclei produced**,

$$\frac{N_{18}(0)}{N_{17}(0)} = 144.7 r.$$

Activity is $A = \lambda N$. Therefore, immediately after irradiation,

$$\frac{A_{18}(0)}{A_{17}(0)} = \frac{\lambda_{18}}{\lambda_{17}} 144.7 r.$$

After time t ,

$$\frac{A_{18}(t)}{A_{17}(t)} = \frac{\lambda_{18}}{\lambda_{17}} 144.7 r e^{(\lambda_{17}-\lambda_{18})t}.$$

Using minutes throughout,

$$\lambda_{18} = \frac{\ln 2}{109.7} = 0.00631857 \text{ min}^{-1},$$

$$\lambda_{17} = \frac{\ln 2}{65/60} = 0.639828 \text{ min}^{-1}.$$

At $t = 5.00 \text{ min}$,

$$e^{(\lambda_{17}-\lambda_{18})t} = 23.7492.$$

Thus the activity ratio at the end of irradiation was

$$\frac{A_{18}(0)}{A_{17}(0)} = \frac{10^5}{23.7492} = 4210.67.$$

Converting this activity ratio into the target mole ratio requires the decay-constant ratio:

$$r = \frac{4210.67}{144.7} \frac{\lambda_{17}}{\lambda_{18}}$$

$$= \frac{4210.67}{144.7} \frac{109.7}{65/60}$$

$$= 2946.64.$$

The corresponding mole fraction is

$$x(\text{H}_2^{18}\text{O}) = \frac{r}{r+1} = 0.9996607.$$

Using approximate isotopic-water molar masses of 20 and 18 g mol^{-1} ,

$$w(\text{H}_2^{18}\text{O}) = \frac{20r}{20r+18}$$

$$= \frac{20(2946.64)}{20(2946.64)+18}$$

$$= 0.9996947.$$

$$\boxed{w(\text{H}_2^{18}\text{O}) \approx 99.97\%}$$

The factor $\lambda_{18}/\lambda_{17}$ is essential here: equal numbers of the two radionuclides would not have equal activities.

5.10 — Decay-corrected labeling yield

The initial and product activities must be compared at the same time. With no chemical loss, the initial sample would have activity

$$A_{\text{available}}(3.5) = 600.0 2^{-3.5/109.7}$$

$$= 586.8766 \text{ MBq}$$

at the end of synthesis.

Therefore, the fraction incorporated into FDG is

$$Y = \frac{528.2}{586.8766} = 0.9000188.$$

$Y = 90.0\%$

5.11 — Radioactivity remaining in the patient

Physical decay and biological elimination independently remove radioactive nuclei from the patient. Their first-order rate constants therefore add:

$$\lambda_{\text{eff}} = \lambda_{\text{physical}} + \lambda_{\text{biological}}.$$

Equivalently,

$$\frac{1}{t_{1/2,\text{eff}}} = \frac{1}{109.7} + \frac{1}{120.0},$$

so

$$t_{1/2,\text{eff}} = 57.3095 \text{ min.}$$

For ten hours, $t = 600 \text{ min}$, the remaining activity is

$$\begin{aligned} A(t) &= 450.0 \, 2^{-600/109.7} \, 2^{-600/120.0} \\ &= 450.0 \, 2^{-600/57.3095} \\ &= 0.3173879 \text{ MBq.} \end{aligned}$$

$A(10 \text{ h}) \approx 0.317 \text{ MBq}$

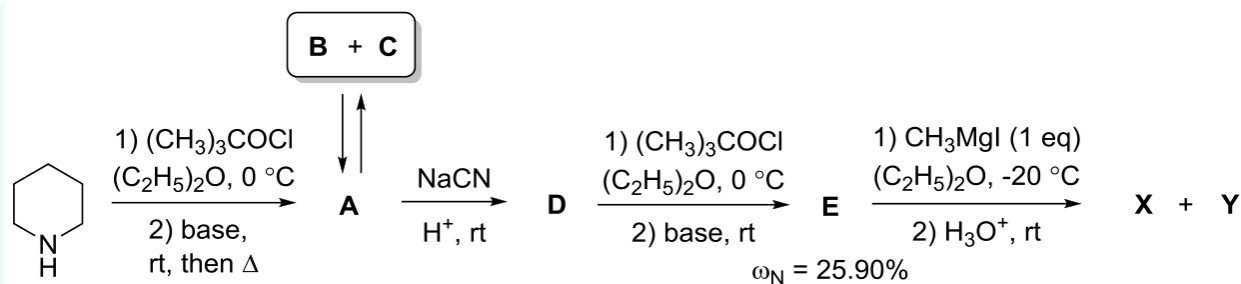
The solution was checked against the official solution.

Problem 6: Bread is the stuff of life

When you pass by the bakery, you are stopped by the smell of freshly baked bread. The hero of one of the novels said on a similar occasion: "If you tell me that this is not perfect, you are my enemy forever." The principle bread flavour component was identified in 1969 as compound **X** which occurs in equilibrium with its tautomer **Y** in a 2 : 1 ratio. Unfortunately, both forms are labile, and after some hours bread has no the same nice smell.



This tautomeric mixture of **X** and **Y** was synthesized in 1993 from piperidine by the reaction sequence given in Scheme 1. It is noteworthy that the initial ratio of **X** and **Y** was 1:4; on standing this ratio gradually changed to an equilibrium one.



Scheme 1.

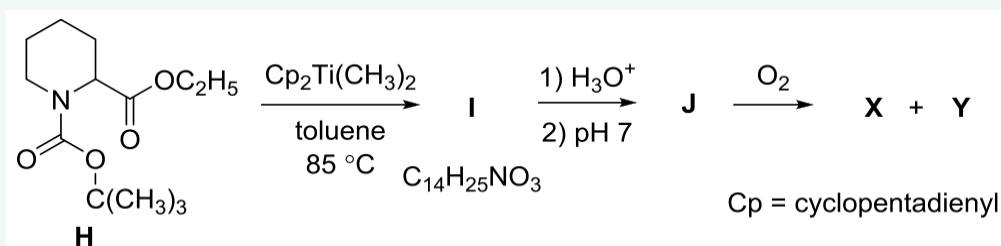
Compound **B** which is characterized by 3-fold axis of symmetry (*i.e.*, rotation by 120° results in a molecule indistinguishable from the original) occurs in equilibrium with its diastereomer **C**. The interconversion of these two forms proceeds *via* intermediate **A** which is also intermediate in **B** and **C** formation as well as their transformation to **D**. Compounds **A**, **B**, and **C** have the same elemental composition: $w_{\text{C}} = 72.24\%$, $w_{\text{H}} = 10.91\%$, $w_{\text{N}} = 16.85\%$.

6.1 Write down the structural formulae of compounds **A - E**, **X**, **Y**.

Treatment of compound **E** with $\text{CH}_3\text{Li} \cdot \text{LiBr}$ complex in $(\text{C}_2\text{H}_5)_2\text{O}$ at 0°C failed to produce the target products **X** and **Y**. Instead, a yellow precipitate **F** was initially formed. Aqueous workup of this precipitate led to the mixture of compound **E** and its tautomer **G**.

6.2 Write down the structural formulae of compounds **F** and **G**.

Another approach to compound **X** is based on the use of pipecolic acid derivative **H**. It was shown that **X** can be synthesized by reaction sequence presented in Scheme 2.



Scheme 2

6.3 Write down the structural formulae of compounds **I** and **J**.

Official English text of the problem.

Answers

• 6.1

Compound	Name and structure
A	1-Piperideine , or 3,4,5,6-tetrahydropyridine: N1=CCCCC1
B	All-cis tripiperideine , the threefold-symmetric cyclic trimer of A: $\text{N12}[\text{C@H}]3\text{CCCCN3}[\text{C@H}]4\text{CCCCN4}[\text{C@H}]1\text{CCCC2}$
C	Tripiperideine with one ring-junction hydrogen reversed , the diastereomer of B: $\text{N12}[\text{C@H}]3\text{CCCCN3}[\text{C@H}]4\text{CCCCN4}[\text{C@@H}]1\text{CCCC2}$

Compound	Name and structure
D	Piperidine-2-carbonitrile: <chem>N#CC1CCCCN1</chem>
E	3,4,5,6-Tetrahydropyridine-2-carbonitrile: <chem>N#CC1=NCCCC1</chem>
X	2-Acetyl-1,4,5,6-tetrahydropyridine , the enamine tautomer: <chem>CC(=O)C1=CCCCN1</chem>
Y	2-Acetyl-3,4,5,6-tetrahydropyridine , the imine tautomer: <chem>CC(=O)C1=NCCCC1</chem>

• 6.2

Compound	Name and structure
F	Lithium salt of 2-cyano-1,4,5,6-tetrahydropyridine , shown in its N-anion resonance form: <chem>[Li+].[N-]1C(C#N)=CCCC1</chem>
G	1,4,5,6-Tetrahydropyridine-2-carbonitrile: <chem>N#CC1=CCCCN1</chem>

• 6.3

Compound	Name and structure
I	tert-Butyl 2-(1-ethoxyethenyl)piperidine-1-carboxylate: <chem>C=C(OCC)C1CCCCN1C(=O)OC(C)(C)C</chem>
J	2-Acetylpiperidine , or 1-(piperidin-2-yl)ethan-1-one: <chem>CC(=O)C1CCCCN1</chem>

For **B**, the three ring-junction carbon-bound hydrogens are on the same face of the central ring. For **C**, two are on one face and the third is on the opposite face. The SMILES specify representative relative configurations.

D is obtained as a racemate. No absolute configuration is specified for the starting material **H**, so none is assigned to **I** or **J**.

Solution

6.1 — Identification of A–E, X and Y

First determine the empirical formula shared by **A**, **B**, and **C**. Using a 100 g sample and conventional atomic molar masses,

$$n_{\text{C}} : n_{\text{H}} : n_{\text{N}} = \frac{72.24}{12.011} : \frac{10.91}{1.008} : \frac{16.85}{14.007} \approx 6.015 : 10.82 : 1.203 \approx 5 : 9 : 1.$$

Thus their common empirical formula is $\text{C}_5\text{H}_9\text{N}$.

Piperidine, N1CCCCC1, has formula $\text{C}_5\text{H}_{11}\text{N}$. Treatment with tert-butyl hypochlorite, CC(C)(C)OCl, first gives **N-chloropiperidine**, ClN1CCCCC1. Base-induced elimination then gives the cyclic imine **A**, with loss of two hydrogen atoms overall. A formal net equation is



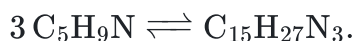
The base neutralizes the hydrogen chloride represented in this equation. Therefore **A** is **1-piperideine**.

Its degree of unsaturation is

$$\text{DBE} = \frac{2(5) + 2 + 1 - 9}{2} = 2,$$

accounted for by one ring and one imine double bond.

Formation and stereochemistry of B and C. Three molecules of **A** undergo reversible cyclic trimerization:



The three imine double bonds become single bonds, and three new intermolecular carbon–nitrogen bonds close a central six-membered ring. Its atoms alternate between nitrogen and carbon. Each alternating N–CH edge is also part of a piperidine ring, completed by a four-methylene bridge.

This addition process changes the molecular formula but preserves the elemental percentages.

To draw the two products precisely:

- Draw the central ring with alternating N and CH atoms, and attach the three four-methylene bridges across alternating N–CH edges.
- For **B**, draw all three central C–H bonds as wedges. The three identical units are related by rotation through 120° .
- For **C**, reverse one of those C–H bonds to a dashed bond. This gives the required diastereomer and removes the threefold symmetry.

The stereochemical SMILES in the answers encode these relative configurations; they do not prescribe a particular chair conformation.

Formation of D. Cyanide adds to the electrophilic carbon of the protonated imine **A**. Net addition of hydrogen cyanide across its imine bond gives **piperidine-2-carbonitrile, D**:



Attack on either face of the planar imine gives racemic **D**. Consumption of **A** also draws **B** and **C** through their equilibria toward **D**.

Formation of E. Repeating the N-chlorination–elimination sequence on **D** removes the N–H hydrogen and the hydrogen on the carbon bearing the cyano group. The result is **E**, with an imine bond between N1 and C2:



The formula $\text{C}_6\text{H}_8\text{N}_2$ gives

$$M_{\text{E}} = 6(12.011) + 8(1.008) + 2(14.007) = 108.144 \text{ g mol}^{-1},$$

and therefore

$$w_{\text{N}} = \frac{28.014 \text{ g mol}^{-1}}{108.144 \text{ g mol}^{-1}} \times 100\% = 25.90\%,$$

in agreement with Scheme 1.

Formation and assignment of X and Y. One equivalent of methylmagnesium iodide adds a methyl group to the nitrile carbon. Acidic hydrolysis converts the resulting nitrogen-containing group into an acetyl group. A balanced net equation for this addition and acidic workup is



The immediate organic product retains the ring imine bond and is therefore **Y, 2-acetyl-3,4,5,6-tetrahydropyridine**.

Transfer of a proton from C3 to nitrogen, accompanied by movement of the double bond from N1–C2 to C2–C3, gives **X**, **2-acetyl-1,4,5,6-tetrahydropyridine**. Both have formula C₇H₁₁NO.

The initially greater abundance of **Y** is consistent with its direct formation from **E**:

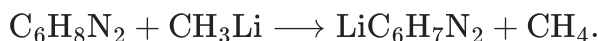
$$(X : Y)_{\text{initial}} = 1 : 4.$$

Subsequent imine–enamine equilibration increases the amount of **X** until

$$(X : Y)_{\text{equilibrium}} = 2 : 1.$$

6.2 — Identification of F and G

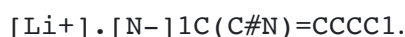
Methylolithium acts as a base toward **E**, removing a proton from C3, adjacent to the imine carbon:



The resulting anion is delocalized. Its C3–carbanion resonance contributor can be written as



Moving the C3 lone pair into the C2–C3 bond and moving the imine π -electron pair onto nitrogen gives the N-anion representation of **F**:



Thus **F** is the lithium salt of the enamine tautomer **G**. The supplied LiBr does not change this organic connectivity.

During aqueous workup, protonation can occur at either end of the delocalized anion:

- Protonation at **C3** regenerates the imine **E**.
- Protonation at **N1** gives the enamine **G**, **1,4,5,6-tetrahydropyridine-2-carbonitrile**.

For either organic tautomer, the balanced formula-level workup is



The ionic SMILES specifies the lithium salt's composition and organic bonding. It does not specify lithium coordination or aggregation in the precipitate.

6.3 — Identification of I and J

The starting material **H** is **ethyl N-Boc-pipecolate**:



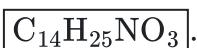
The titanocene reagent in Scheme 2 performs **Petasis methylenation** of the side-chain ester carbonyl. It replaces that carbonyl oxygen with a terminal methylene group while retaining the ethoxy group on the same carbon.

Consequently, **I** contains the substituent



at C2 of the N-Boc-protected piperidine ring. It is **tert-butyl 2-(1-ethoxyethenyl)piperidine-1-carboxylate**.

The formula provides an independent check: replacing one oxygen of **H**, C₁₃H₂₃NO₄, by CH₂ gives exactly the stated formula



Acid treatment has two consequences:

1. Hydrolysis of the enol ether produces the methyl ketone.
2. Removal of the Boc protecting group exposes the secondary amine.

After the stated pH adjustment, the resulting structure is **J**, **2-acetylpiperidine**.

A balanced net equation for hydrolysis and Boc removal, representing the final organic product as its free base, is



The carbon-containing by-products are ethanol, CCO ; carbon dioxide, $\text{O}=\text{C}=\text{O}$; and 2-methylpropene, $\text{C}=\text{C}(\text{C})\text{C}$.

Finally, oxygen oxidizes the secondary amino ketone **J** to the ring imine **Y** by removing the N–H hydrogen and the C2 hydrogen. The balanced substrate oxidation half-reaction is



The resulting **Y** undergoes the imine–enamine tautomerization established in part **6.1**, giving the mixture of **X** and **Y**.

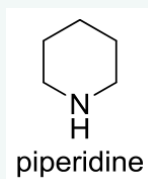
The answers were checked against the official answers published by the organisers.

Problem 7: Not by bread alone

Pomegranate is called in Azerbaijan, which is famous for its vegetables, as the “king of all fruits”. Pomegranate is honored in various religions as a “fruit of Paradise”, symbol of righteousness, wealth, hope for eternal life.

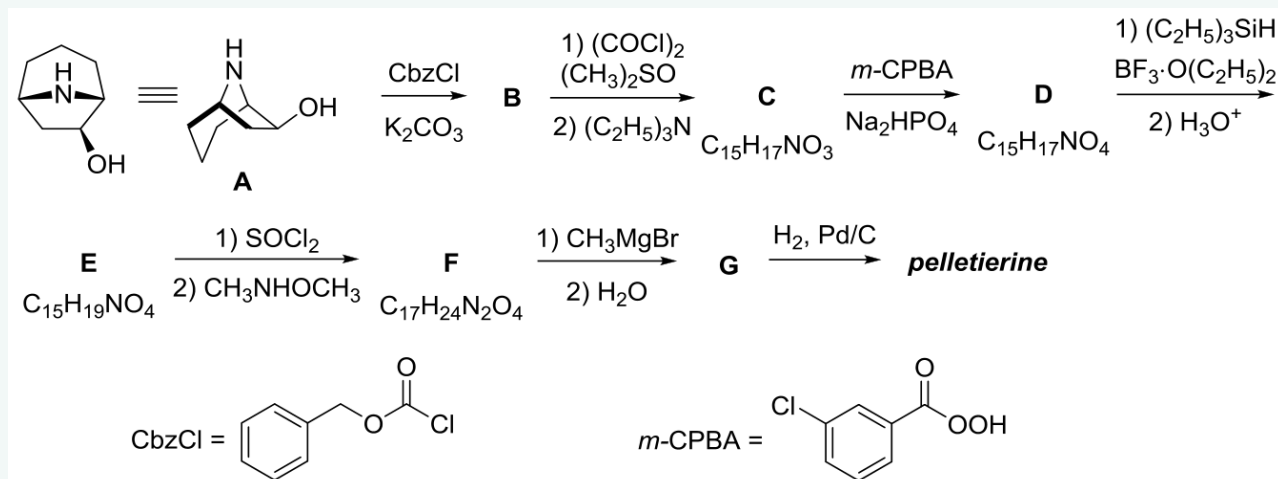


In 1878 alkaloid **pelletierine** was isolated from the bark of pomegranate tree (*Punica granatum* L., *Lythraceae*). This alkaloid is traditionally used as an anti-helminthic drug. Initially X_W (3-(piperidin-2-yl)propanal) was incorrectly proposed for pelletierine. But now it is accepted that natural pelletierine is (S)-1-(piperidin-2-yl)propan-2-one (X_S).



7.1 Write down the structural formulae of X_W and X_S (the latter – with the stereochemical information).

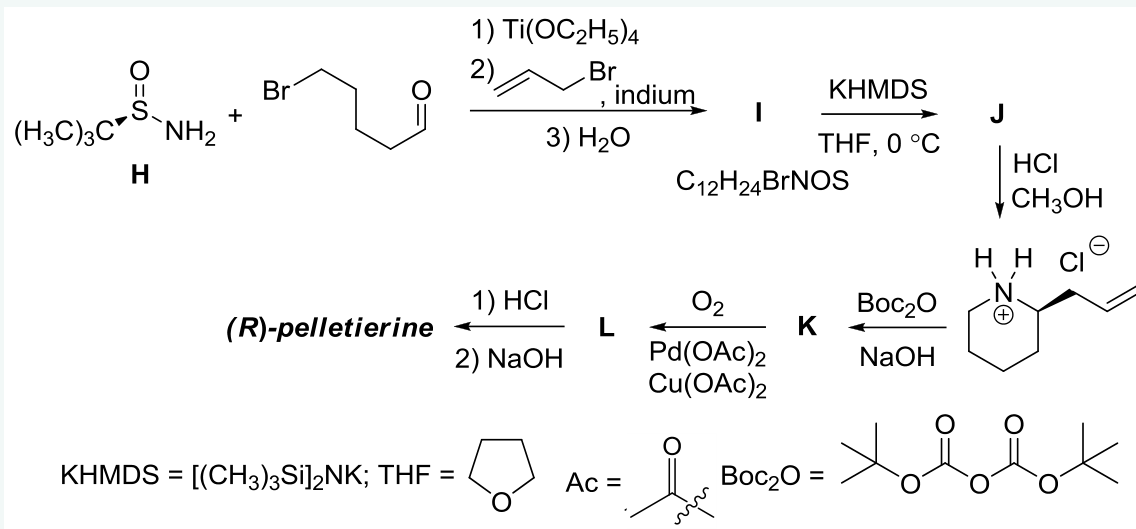
The synthesis of natural pelletierine (X_S) based on the transformation of nortropanol **A** was recently described.



7.2 Write down the structural formulae of compounds **B - G** with the stereochemical information.

7.3 Nortropanol **A** was used in this reaction as a single stereoisomer. How many stereoisomers can exist for compound **A** (including **A**)? Ignore nitrogen chirality.

Enantiomer of X_S was synthesized using chiral *tert*-butanesulfinamide (**H**):



7.4 Write down the structural formulae of compounds **I - L** with the stereochemical information.

Official English text of the problem.

Answers

Cbz means benzyloxycarbonyl, and Boc means *tert*-butoxycarbonyl. The descriptor R_S denotes an *R* configuration at sulfur.

• 7.1

Compound	Name	SMILES
X_W	3-(Piperidin-2-yl)propanal; stereochemistry unspecified	O=CCCC1CCCCN1

Compound	Name	SMILES
X_S	(S)-1-(Piperidin-2-yl)propan-2-one, natural pelletierine	<chem>CC(=O)C[C@@H]1CCCCN1</chem>

• 7.2

Compound	Name	Isomeric SMILES
B	Benzyl (1S,5R,6S)-6-hydroxy-8-azabicyclo[3.2.1]octane-8-carboxylate	<chem>O=C(OCc1ccccc1)N1[C@H]2CCC[C@@H]1[C@@H](O)C2</chem>
C	Benzyl (1S,5R)-6-oxo-8-azabicyclo[3.2.1]octane-8-carboxylate	<chem>O=C(OCc1ccccc1)N1[C@H]2CCC[C@@H]1C(=O)C2</chem>
D	Benzyl (1S,5S)-3-oxo-2-oxa-9-azabicyclo[3.3.1]nonane-9-carboxylate	<chem>O=C(OCc1ccccc1)N1[C@H]2CCC[C@@H]1OC(=O)C2</chem>
E	2-[(2S)-1-(benzyloxycarbonyl)piperidin-2-yl]acetic acid	<chem>O=C(O)C[C@@H]1CCCCN1C(=O)OCc1ccccc1</chem>
F	N-Methoxy-N-methyl-2-[(2S)-1-(benzyloxycarbonyl)piperidin-2-yl]acetamide, the Weinreb amide of E	<chem>CN(OC)C(=O)C[C@@H]1CCCCN1C(=O)OCc1ccccc1</chem>
G	Benzyl (2S)-2-(2-oxopropyl)piperidine-1-carboxylate, N-Cbz-(S)-pelletierine	<chem>CC(=O)C[C@@H]1CCCCN1C(=O)OCc1ccccc1</chem>

• 7.3 There are **four stereoisomers**, comprising **two enantiomeric pairs**.

• 7.4

Compound	Name	Isomeric SMILES
I	(R_S)-N-[(4R)-8-bromooct-1-en-4-yl]-2-methylpropane-2-sulfinamide	<chem>C=CC[C@@H](CCCCBr)N[S@](=O)C(C)(C)C</chem>
J	(2R, R_S)-2-Allyl-1-(tert-butylsulfinyl)piperidine	<chem>C=CC[C@H]1CCCCN1[S@](=O)C(C)(C)C</chem>
K	tert-Butyl (2R)-2-(prop-2-en-1-yl)piperidine-1-carboxylate	<chem>C=CC[C@H]1CCCCN1C(=O)OC(C)(C)C</chem>
L	tert-Butyl (2R)-2-(2-oxopropyl)piperidine-1-carboxylate, N-Boc-(R)-pelletierine	<chem>CC(=O)C[C@H]1CCCCN1C(=O)OC(C)(C)C</chem>

Solution

7.1 — The proposed and actual structures

In X_W , carbon 3 of propanal is attached to carbon 2 of piperidine. Thus the substituent on the piperidine ring is $-\text{CH}_2-\text{CH}_2-\text{CHO}$. No configuration is specified for its stereogenic ring carbon.

In X_S , carbon 1 of propan-2-one is attached to carbon 2 of piperidine. Its side chain is therefore $-\text{CH}_2-\text{C}(=\text{O})-\text{CH}_3$.

At the stereogenic carbon of X_S , the CIP priorities are:

nitrogen > side-chain carbon > ring methylene carbon > hydrogen.

The two carbon substituents initially tie, but the side-chain path reaches the carbonyl oxygen atoms before the ring path reaches any heteroatom. Natural pelletierine has the specified S configuration, encoded in CC(=O)C[C@H]1CCCCN1.

7.2 — Identification of B–G

For **A–C**, use the nortropane numbering: the bridgeheads are C1 and C5, nitrogen is position 8, and the shorter carbon bridge runs C1–C7–C6–C5. The starting alcohol **A** is (1*S*,5*R*,6*S*)-8-azabicyclo[3.2.1]octan-6-ol, N1[C@H]2CCC[C@@H]1[C@H](O)C2.

A → B: protection of nitrogen.

Benzyl chloroformate, O=C(Cl)OCc1ccccc1, converts the secondary amine into its Cbz carbamate. Potassium carbonate neutralizes the acid formed. The alcohol remains intact, and all three carbon configurations are retained.

Thus **B** is the N-Cbz derivative of **A**.

B → C: Swern oxidation.

The combination of oxalyl chloride, dimethyl sulfoxide and triethylamine oxidizes the secondary alcohol to a ketone.

C6 becomes trigonal planar, so its stereocentre disappears. The configurations at C1 and C5 remain unchanged. Loss of two hydrogen atoms gives the stated formula $\text{C}_{15}\text{H}_{17}\text{NO}_3$.

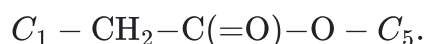
C → D: Baeyer–Villiger oxidation.

The peracid inserts an oxygen atom into a bond adjacent to the ketone. The nitrogen-bearing bridgehead C5 migrates preferentially over the competing methylene carbon C7.

Consequently, the short bridge changes from



to



This gives the ring-expanded bicyclic lactone **D**, with formula $\text{C}_{15}\text{H}_{17}\text{NO}_4$.

Migration occurs with retention of spatial configuration at the migrating carbon. Its CIP descriptor changes because insertion of oxygen changes the priority order; this does **not** represent inversion. In the numbering of the expanded bicyclic system, **D** has configuration (1*S*, 5*S*).

D → E: reductive opening of the lactone bridge.

The lactone contains a carbon bonded to both nitrogen and oxygen—the former C5. Lewis-acid activation followed by hydride delivery replaces its carbon–oxygen bond with a carbon–hydrogen bond.

The bridge opens, and aqueous workup gives the carboxylic acid. The former C5 becomes a methylene group, while the former C1 remains stereogenic. Its configuration is S .

The product is therefore **E**, the N-Cbz-protected (*S*)-piperidine-2-acetic acid derivative. The change



expresses the substrate formula change: two hydrogen atoms are added overall.

E → F: formation of a Weinreb amide.

Thionyl chloride activates the carboxylic acid as its acid chloride. Reaction with N,O-dimethylhydroxylamine, CNOC, then produces the N-methoxy-N-methylamide **F**.

The side chain becomes $-\text{CH}_2-\text{C}(=\text{O})-\text{N}(\text{CH}_3)-\text{OCH}_3$. Its formula is $\text{C}_{17}\text{H}_{24}\text{N}_2\text{O}_4$, matching the problem. The ring stereocentre remains *S*.

F → G: selective formation of the methyl ketone.

Methylmagnesium bromide adds a methyl group to the Weinreb amide carbonyl. Coordination of magnesium to the two oxygen atoms stabilizes a five-membered chelated intermediate. This prevents release of the ketone, and hence further addition to it, before aqueous workup.

Hydrolysis gives the side chain $-\text{CH}_2-\text{C}(=\text{O})-\text{CH}_3$. Thus **G** is N-Cbz-(*S*)-pelletierine.

G → X_S: removal of Cbz.

Hydrogenolysis removes the benzyl carbamate without changing the carbon stereocentre. The balanced overall equation is



The products are natural pelletierine *X_S*, toluene (Cc1ccccc1) and carbon dioxide (O=C=O).

The formulas of **C**, **D**, **E** and **F** independently obtained from the structures agree with all four formulas printed in the scheme.

7.3 — Number of stereoisomers of A

Ignoring nitrogen chirality, **A** has three stereogenic carbon atoms: C1, C5 and C6. However, the two bridgehead configurations cannot vary independently: their relative configuration is constrained by the short bridges.

There are two allowed bridgehead configurations, and for each there are two configurations at the alcohol-bearing carbon:

$$N_{\text{stereoisomers}} = 2 \times 2 = \boxed{4}.$$

For the 8-azabicyclo[3.2.1]octan-6-ol skeleton, these are:

Configuration	Isomeric SMILES
(1 <i>S</i> , 5 <i>R</i> , 6 <i>S</i>), A	N1[C@H]2CCC[C@@H]1[C@@H](O)C2
(1 <i>R</i> , 5 <i>S</i> , 6 <i>R</i>), enantiomer of A	N1[C@@H]2CCC[C@H]1[C@H](O)C2
(1 <i>S</i> , 5 <i>R</i> , 6 <i>R</i>), the C6 epimer of A	N1[C@H]2CCC[C@@H]1[C@H](O)C2
(1 <i>R</i> , 5 <i>S</i> , 6 <i>S</i>), enantiomer of that epimer	N1[C@@H]2CCC[C@H]1[C@@H](O)C2

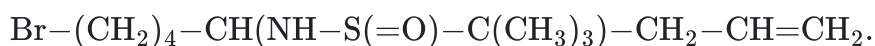
Thus the four structures form two enantiomeric pairs. Alternative conformations do not count as additional stereoisomers.

7.4 — Identification of I–L

Formation of I: condensation followed by asymmetric allylation.

The depicted auxiliary **H** is (*R*)-tert-butanefulfonamide, CC(C)(C)[S@](N)=O.

Titanium ethoxide promotes its condensation with 5-bromopentanal, $\text{O}=\text{CCCCCBr}$, forming a sulfinimine. Indium-mediated addition of allyl bromide, $\text{C}=\text{CCBr}$, introduces the allyl group at the former aldehyde carbon. After workup, **I** has the connectivity



The carbon stereocentre is *R*, and the sulfur retains its *R* configuration. The carbon configuration can also be established directly from the downstream hydrochloride drawn in the problem: neither the intervening cyclization nor auxiliary removal changes the configuration of that carbon.

Counting atoms gives $\text{C}_{12}\text{H}_{24}\text{BrNOS}$, as required.

I → J: intramolecular substitution.

KHMDS removes the sulfonamide proton. The resulting nitrogen nucleophile attacks the terminal carbon bearing bromine by an intramolecular $\text{S}_{\text{N}}2$ reaction.

The ring contains nitrogen, the stereogenic carbon, and four methylene groups: a six-membered piperidine ring. Substitution occurs at an achiral terminal methylene carbon, so the existing *R* carbon centre is retained. Sulfur also retains its configuration.

Thus **J** is the N-tert-butylsulfinyl-protected (R)-2-allylpiperidine.

J → K: exchange of nitrogen protecting groups.

Methanolic hydrochloric acid cleaves the nitrogen–sulfur bond. It gives the depicted (2R)-2-allylpiperidinium chloride, $\text{C}=\text{CC}[\text{C@H}]1\text{CCCC}[\text{NH}_2^+]1.[\text{Cl}^-]$.

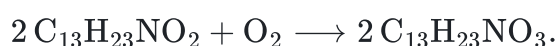
Base releases the amine, and di-tert-butyl dicarbonate introduces Boc protection, giving **K**. The carbon stereocentre remains *R*.

K → L: Wacker oxidation.

The palladium/copper system oxidizes the terminal alkene to a methyl ketone:



Thus **L** is N-Boc-(R)-pelletierine. The balanced net oxidation, with oxygen as the terminal oxidant, is



No bond at the stereogenic ring carbon is broken, so its configuration remains *R*.

Finally, hydrochloric acid removes Boc protection, and sodium hydroxide releases **(R)-pelletierine**, (R)-1-(piperidin-2-yl)propan-2-one, $\text{CC}(=\text{O})\text{C}[\text{C@H}]1\text{CCCCN}1$. This is the enantiomer of natural *X_S*.

The answers were checked against the official answers published by the organisers.

Problem 8: Oil for Life and Life after Oil

Azerbaijan is known for its vast oil and gas fields. The first drilling for oil was done in Bibi-Heybat in 1846, 13 years before establishment of the first commercial oil well in Pennsylvania (USA). This remarkable date in the history of Azerbaijan is regarded as a starting point of contemporary oil industry, the leading sector of today's world economy.



Currently, on-land and shelf sea oil production is being developed in Azerbaijan. Though serious precautions are taken, there is always a risk of hydrocarbon pollution of the environment during production, transportation, and processing of oil. In this task we will consider diverse technologies of oil spills clean up and specific features of metabolic pathways involved.

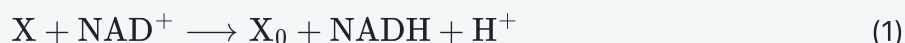
Application of complex solvents (dispersants) leading to capture of marine oil spills is among most promising clean up approaches. Organic substance **X** (11.94 % of **H** by mass) is a typical component of such dispersants. Safety of **X** to human is fiercely debated. **X1** (54.53 % of carbon by mass) composed of three elements and excreted with urine is the major metabolite of **X** in humans. The numbers of atoms of different elements in **X1** are three consecutive terms of a geometric progression (n, nq, nq^2) , whereas the sum of these numbers does not exceed 25.

8.1 Decide on the relationship (tick the correct variant) between the numbers of carbon and oxygen atoms in **X1**.

$n(C) > n(O)$	$n(C) < n(O)$	$n(C) = n(O)$	Data insufficient
☐	☐	☐	☐

8.2 Derive the empirical formula of **X1** (hereafter always show your work where required). Be sure you prove the answer by calculations.

The biotransformation of **X** into **X1** occurs in two enzymatically catalyzed steps according to the hereunder reaction balanced equations (NAD^+ and NADH are the oxidized and reduced forms of nicotinamide adenine dinucleotide, respectively):



8.3 Derive the molecular formula of **X**.

A minor metabolic transformation of **X** is catalyzed by cytochrome P450-dependent monooxygenase. This reaction leads to two compounds **X2** (51.56 % of oxygen and 9.74 % of hydrogen by mass) and **X3**.

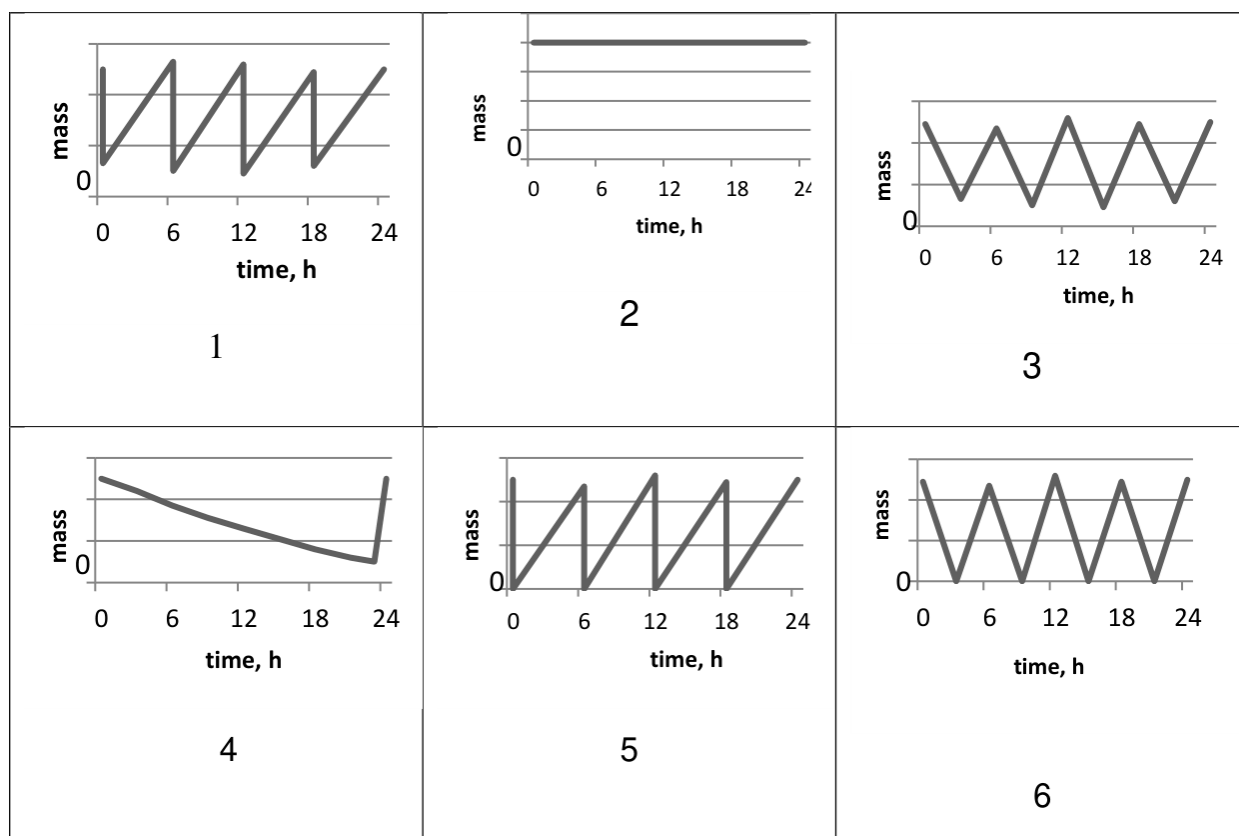
8.4 Derive the molecular formula of **X2** and draw its structure.

X contains only primary and secondary carbon atoms. **X0** and **X3** contain common functional group.

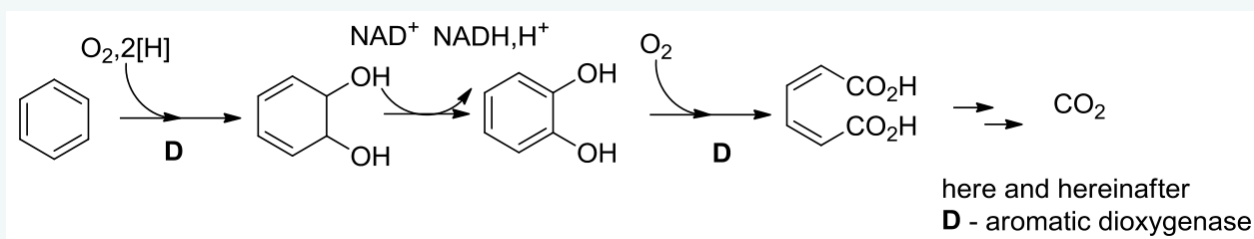
8.5 Draw the structural formulae of **X**, **X1**, and **X3**.

In a medical study, personnel permanently exposed to **X**-based solvents without proper protection was found to have a stationary concentration of **X** in blood.

8.6 **X1** is excreted with urine. Choose the graph of **X1** daily mass content in the body of a volunteer participated in this experiment. Write down the number of the correct graph.

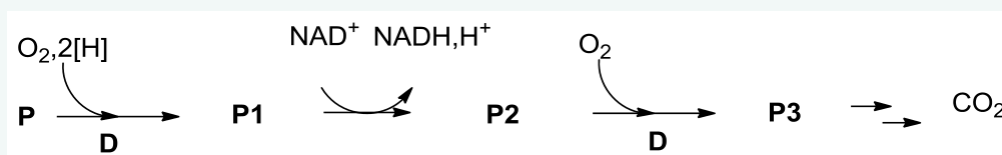


The use of different bacteria is also considered as a promising way for the removal of hydrocarbon (even aromatic) contaminants from sea water and soil. Under aerobic conditions, benzene undergoes biodegradation as follows (first three steps are balanced):



here and hereinafter
D - aromatic dioxygenase

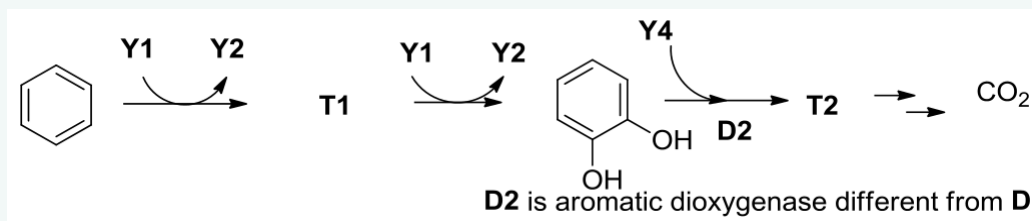
Under the same conditions, a monocyclic aromatic hydrocarbon **P** (91.25 % of carbon by mass) undergoes the following transformation (first three steps are balanced):



P3 gives a positive iodoform test. A 100 mg sample of **P3** requires 6.41 cm³ of KOH ($c = 0.100 \text{ mol dm}^{-3}$) solution for complete neutralization.

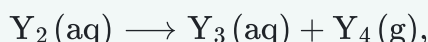
8.7 Derive the structures of **P–P3**. Give the most stable tautomer of **P3**.

Microorganisms *Alicyclophilus* are capable of biodegradation of aromatic hydrocarbons even in soil. The process requires a suitable electron acceptor such as inorganic anion **Y1** (first three steps are balanced).



D2 is aromatic dioxygenase different from **D**

The intermediate anion **Y2** is enzymatically decomposed according to the balanced reaction equation:



wherein each of **Y3** and **Y4** is composed of atoms of only one element. **T2** does not contain two identical oxygen-containing functional groups. **T2** gives a precipitate when treated with the ammonia solution of Ag_2O , whereas **Y3** does not.

8.8 Deduce and give formulas of **Y1-Y4**. Draw the structures of **T1-T2**. Give the most stable tautomer of **T2**.

Official English text of the problem.

Answers

- **8.1:** Tick $n(C) > n(O)$.
- **8.2:** The empirical formula of **X1** is C_2H_4O .
- **8.3:** The molecular formula of **X** is $C_6H_{14}O_2$.
- **8.4:** **X2** is ethane-1,2-diol (ethylene glycol), $C_2H_6O_2$, OCCO.
- **8.5:** **X:** 2-butoxyethan-1-ol, CCCCOCCO; **X1:** 2-butoxyacetic acid, CCCCOCC(=O)O; **X3:** butanal, CCC=O.
- **8.6:** Graph 1.
- **8.7:** **P:** toluene, Cc1ccccc1; **P1:** cis-3-methylcyclohexa-3,5-diene-1,2-diol, O[C@H]1[C@@H](O)C(C)=CC=C1 (one cis enantiomer shown); **P2:** 3-methylbenzene-1,2-diol (3-methylcatechol), Oc1c(O)c(C)ccc1; **P3:** 2-hydroxy-6-oxohepta-2,4-dienoic acid, CC(=O)C=CC(=O)C(=O)O. I select this conjugated enol tautomer.
- **8.8:** **Y1:** chlorate, ClO_3^- , $[O-]Cl(=O)=O$; **Y2:** chlorite, ClO_2^- , $[O-]Cl=O$; **Y3:** chloride, Cl^- , $[Cl-]$; **Y4:** dioxygen, O_2 , $O=O$. **T1:** phenol, Oc1ccccc1; **T2:** 2-hydroxy-6-oxohexa-2,4-dienoic acid (2-hydroxymuconic semialdehyde), $O=CC=CC(=O)C(=O)O$. I likewise select its conjugated enol tautomer.

Solution

The calculations below use atomic molar masses 12.01 , 1.008 , and 16.00 g mol^{-1} for carbon, hydrogen, and oxygen, respectively.

8.1

Let the numbers of carbon and oxygen atoms in **X1** be c and o . If $c \leq o$, even omitting the mass of the third element would give

$$w(\text{C}) < \frac{12.01c}{12.01c + 16.00o} \leq \frac{12.01}{12.01 + 16.00} = 0.4288.$$

This contradicts the measured carbon mass fraction 0.5453 . Therefore,

$$\boxed{c > o}.$$

The first box must be ticked.

8.2

Write the C/H/O composition as $\text{C}_c\text{H}_h\text{O}_o$. Its carbon mass fraction satisfies

$$\frac{12.01c}{12.01c + 1.008h + 16.00o} = 0.5453.$$

The geometric-progression condition can be checked exhaustively without an unbounded search. In increasing order, three integer terms of a geometric progression have the form

$$kr^2, \quad krs, \quad ks^2,$$

where r, s are coprime positive integers and $s \geq r$. The atom-count limit requires

$$k(r^2 + rs + s^2) \leq 25.$$

Equal terms are excluded by $c > o$. The remaining primitive triples are only

$$(1, 2, 4), \quad (1, 3, 9), \quad (1, 4, 16), \quad (4, 6, 9).$$

For each triple, assigning its entries to c, h, o , subject to $c > o$, gives:

Primitive atom-count triple	Possible carbon percentages with $c > o$
(1, 2, 4)	54.53 , 59.27, 72.73
(1, 3, 9)	58.97, 68.80, 85.03
(1, 4, 16)	59.92, 74.72, 90.56
(4, 6, 9)	49.65, 51.94, 60.68

The unique matching assignment is

$$c : h : o = 2 : 4 : 1.$$

Indeed,

$$100 w(\text{C}) = 100 \frac{2(12.01)}{2(12.01) + 4(1.008) + 16.00} = 54.526\% \approx 54.53\%.$$

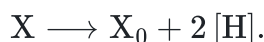
Thus

$$\boxed{\text{empirical formula of X1} = \text{C}_2\text{H}_4\text{O}}.$$

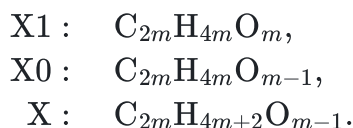
Its molecular formula is $C_{2m}H_{4m}O_m$. Since the molecule contains $7m \leq 25$ atoms, m can only be 1, 2, or 3. An empirical formula alone does not specify a molecular structure or a unique SMILES.

8.3

In reaction (1), **X** loses two hydrogen atoms:



Reaction (2) adds one oxygen atom to **X0**, without changing its total hydrogen count. Consequently,



Using the hydrogen percentage of **X**,

$$\frac{1.008(4m + 2)}{12.01(2m) + 1.008(4m + 2) + 16.00(m - 1)} = 0.1194.$$

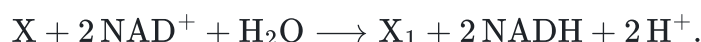
This gives $m = 3.00$, within the rounding of the analytical data. Therefore,



The check is

$$100 w(H) = 100 \frac{14(1.008)}{118.172} = 11.9419\% \approx 11.94\%.$$

The combined balanced oxidation is



8.4

The carbon percentage of **X2** is

$$100 - 51.56 - 9.74 = 38.70\%.$$

For a 100 g sample:

Element	Amount of atoms
Carbon	$38.70/12.01 = 3.222 \text{ mol}$
Hydrogen	$9.74/1.008 = 9.663 \text{ mol}$
Oxygen	$51.56/16.00 = 3.223 \text{ mol}$

Thus the empirical ratio is

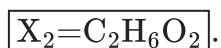
$$C : H : O = 1 : 3 : 1,$$

and the molecular formula is initially $C_mH_{3m}O_m$.

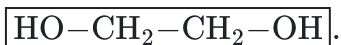
For an ordinary neutral, closed-shell C/H/O compound,

$$DBE = \frac{2m + 2 - 3m}{2} = 1 - \frac{m}{2}$$

must be a nonnegative integer. Hence $m = 2$, giving



The main oxidation sequence identifies a primary alcohol in **X**. P450-catalyzed oxidative ether cleavage releases an alcohol fragment while preserving that original alcohol group. The resulting two-carbon diol is therefore **ethane-1,2-diol**, OCCO:



The required drawing is a two-carbon single-bonded chain with one hydroxyl group on each carbon.

Its calculated composition is

$$w(\text{O}) = 51.556\%, \quad w(\text{H}) = 9.744\%,$$

in agreement with the data.

8.5

The two-step oxidation



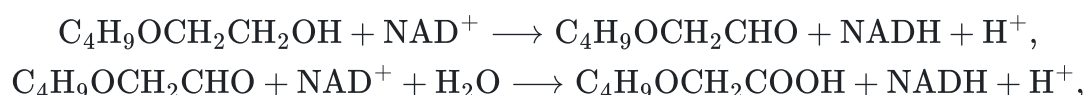
identifies **X0** as an aldehyde. Thus **X3**, which shares its functional group, must also be an aldehyde.

The ethylene glycol fragment contains two of the six carbons of **X**. The other fragment therefore contains four carbons. A straight butyl ether gives butanal on oxidative cleavage. A sec-butyl ether would instead give a ketone, while branched isobutyl or tert-butyl structures would introduce a tertiary carbon atom into **X**.

The structures are therefore:

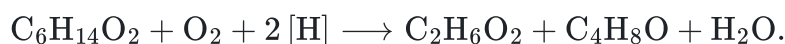
Label	Name and SMILES	Condensed structure
X	2-Butoxyethan-1-ol, CCCCOCCO	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2-\text{O}-\text{CH}_2\text{CH}_2\text{OH}$
X0	2-Butoxyethanal, CCCCOCC=O	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2-\text{O}-\text{CH}_2\text{CHO}$
X1	2-Butoxyacetic acid, CCCCOCC(=O)O	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2-\text{O}-\text{CH}_2\text{COOH}$
X3	Butanal, CCC=O	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CHO}$

The structural oxidation equations are

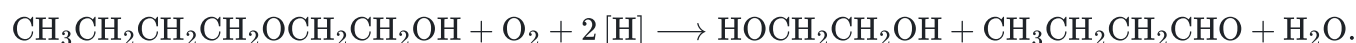


where every C_4H_9 group is the straight-chain butyl group.

Using the problem's notation $2[\text{H}]$ for reducing hydrogen equivalents, the balanced monooxygenase reaction is



Structurally,



8.6

A stationary blood concentration of **X** supports approximately constant production of **X1**. Between urinations, the total amount of **X1** inside the body, including urine retained in the bladder, increases. Urination removes accumulated metabolite rapidly.

The amount does not fall to zero because metabolite remains in blood, tissues, and residual urine. The required graph therefore has gradual increases and abrupt decreases to nonzero minima:

Graph 1.

8.7

First determine the hydrocarbon composition:

$$n(\text{C}) : n(\text{H}) = \frac{91.25}{12.01} : \frac{8.75}{1.008} \approx 7 : 8.$$

Thus **P** has molecular formula $\text{C}_{7k}\text{H}_{8k}$.

The balanced first three steps add two oxygen atoms, remove the two newly supplied hydrogen atoms, and then add two more oxygen atoms. Therefore,



The neutralization consumes

$$n(\text{KOH}) = (0.100 \text{ mol dm}^{-3})(6.41 \times 10^{-3} \text{ dm}^3) = 6.41 \times 10^{-4} \text{ mol}.$$

The equivalent molar mass is

$$\frac{0.100 \text{ g}}{6.41 \times 10^{-4} \text{ mol}} = 156.0 \text{ g mol}^{-1}.$$

If **P3** has a carboxyl groups,

$$M(\text{P3}) = 156.0a \text{ g mol}^{-1}.$$

Four oxygen atoms allow at most two carboxyl groups, so the possibilities are $a = 1$ or 2 . Meanwhile,

$$M(\text{P3}) = 92.134k + 64.00.$$

For $a = 1$, $k \approx 1$; for $a = 2$, $k \approx 2.69$, which is not an integer. Consequently,



and **P3** has one carboxyl group. The monocyclic aromatic hydrocarbon **P** is **toluene**, Cc1ccccc1.

For this oxidative ring-cleavage product, the positive iodoform test identifies a methyl ketone group, CH_3CO^- . The general balanced test reaction is



The yellow precipitate is **iodoform**, $\text{IC}(\text{I})\text{I}$.

To obtain a methyl ketone at the opened end of the aromatic ring, the methyl-bearing ring carbon must be adjacent to a hydroxyl-bearing carbon. This identifies **P2** as **3-methylcatechol**, Oc1c(O)c(C)ccc1.

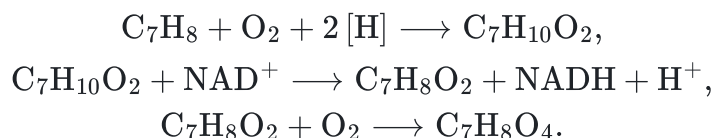
Number the hydroxyl-bearing ring carbons 1 and 2 and the methyl-bearing carbon 3. Cleavage of the bond between carbons 2 and 3 gives



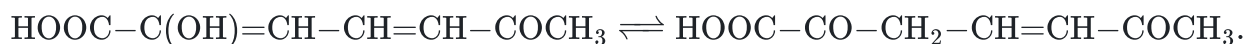
This is **2-hydroxy-6-oxohepta-2,4-dienoic acid**, CC(=O)C=CC(=O)C(=O)O. It has exactly the required carboxyl group and methyl ketone.

Working backward, **P1** is **cis-3-methylcyclohexa-3,5-diene-1,2-diol**, O[C@H]1[C@@H](O)C(C)=CC=C1. Draw a six-membered ring with hydroxyl groups at positions 1 and 2 on the same face, a methyl group at position 3, and double bonds at 3–4 and 5–6. The displayed SMILES represents one cis enantiomer; the problem does not specify the absolute configuration selected by the enzyme.

The three balanced transformations are



For the requested tautomer, I select the conjugated enol shown above: its two carbon–carbon double bonds form a continuous conjugated system with the terminal carbonyl groups. Its direct keto tautomer is **2,6-dioxohept-4-enoic acid**, CC(=O)C=CCC(=O)C(=O)O:



8.8

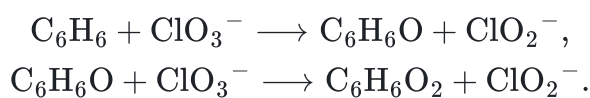
Y4 supplies the oxygen used by the aromatic dioxygenase, so it is **dioxygen**, O=O.

The relevant oxygen-generating decomposition of an aqueous inorganic anion is



Thus **Y2** is chlorite and **Y3** is chloride. The equation balances both atoms and charge. It is an internal redox reaction: chlorine changes from oxidation state +3 to −1, while the two oxygen atoms change from −2 to 0.

The preceding electron acceptor is **chlorate**, ClO3-. Its reduction to chlorite transfers one oxygen atom to the organic substrate at each step:



Therefore **T1** is **phenol**, Oc1ccccc1, and the next intermediate is **benzene-1,2-diol (catechol)**, Oc1ccccc1O.

The ion assignments, including SMILES, are:

Label	Identity	Formula	SMILES
Y1	Chlorate	<chem>ClO3-</chem>	<chem>[O-]Cl(=O)=O</chem>
Y2	Chlorite	<chem>ClO2-</chem>	<chem>[O-]Cl=O</chem>
Y3	Chloride	<chem>Cl-</chem>	<chem>[Cl-]</chem>
Y4	Dioxygen	<chem>O2</chem>	<chem>O=O</chem>

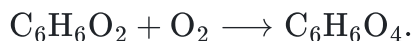
The localized chlorine–oxygen bond orders in these SMILES are resonance representations. The conventional dioxygen SMILES does not encode its ground-state triplet spin.

For **T2**, ordinary cleavage between the two hydroxyl-bearing carbons would produce two carboxyl groups, contradicting the stated absence of two identical oxygen-containing functional groups. Instead, **D2** performs cleavage adjacent to the catechol diol unit. The resulting chain has one carboxyl group and an aldehyde end:

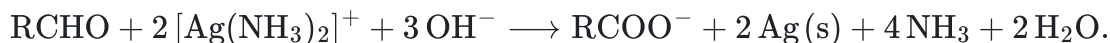


This is **2-hydroxy-6-oxohexa-2,4-dienoic acid**, also called **2-hydroxymuconic semialdehyde**, O=CC=CC(=O)C(=O)O.

The ring-cleavage balance is



Its aldehyde explains the positive Tollens test:



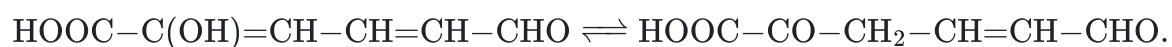
The precipitated material is metallic silver, $[\text{Ag}]$. The oxidant is **diamminesilver(I)**, $[\text{NH}_3] \rightarrow [\text{Ag}^+] \leftarrow [\text{NH}_3]$, with a linear nitrogen–silver–nitrogen coordination geometry.

Chloride does not reduce the silver reagent. In ammoniacal solution, silver chloride can dissolve through complex formation:



This accounts for the intended negative precipitation observation for **Y3**.

As for **P3**, I select the conjugated enol representation of **T2**. Its direct keto tautomer is **2,6-dioxohex-4-enoic acid**, $\text{O}=\text{CC}=\text{CCC}(=\text{O})\text{C}(=\text{O})\text{O}$:



The solution was checked against the official solution.