

Challenge POTD Compilation

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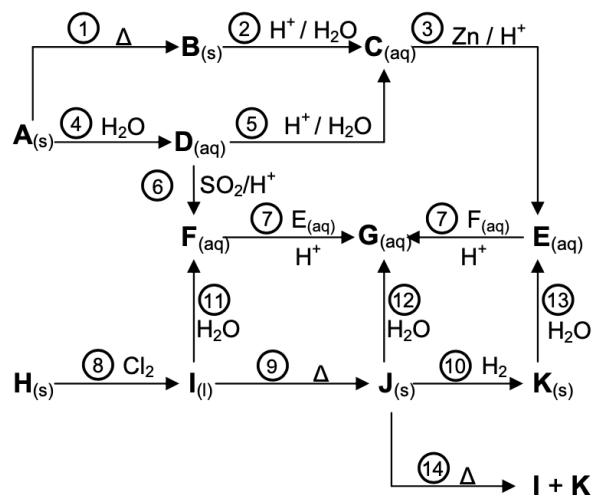
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1 POTD 1: Transition Metal Puzzle

This is problem 2 of the 2008 IChO Preparatory Problems

Compound **A** is a stable salt of metal H. It contains 11.97 %N, 3.45 %H and 41.03 %O (mass fractions), besides the metal. The following chart describes some reactions starting from **A** and **H**. The necessary reactants are displayed above the arrows (Δ signifies heating). All substances tagged with a letter contain the metal, but none of the by-products do. (When a substance is labeled as dissolved in water, then it is ionic and you have to show only the ion containing the metal.)



- Identify the substances **A-K** and write down all the equations 1-14.
- Select the redox processes from the reactions.
- Select those compounds from A-K that are not expected to have unpaired electrons.
- On the basis of the above chart propose a reaction to obtain **G** starting from **F**, without using **E**.
- Compound **B** is industrially very important. Show a reaction where its presence is indispensable. What role does it play?
- What percentage of product **I** contains ^{35}Cl if chlorine gas containing 99 % ^{37}Cl and 1 % ^{35}Cl is used in reaction 8?
- What percentage of **J** produced from this sample of **I** contains ^{35}Cl ?

2 POTD 2: Introduction to Harmonic Oscillator

This is problem 4 of the 2017 IChO Preparatory Problems

For the vibrational motion of a diatomic molecule using a harmonic oscillator model, the allowed vibrational energy levels can be described as:

$$E_\nu = \left(\nu + \frac{1}{2} \right) h\nu \quad ; \nu = 0, 1, 2, \dots$$

where ν is the vibrational quantum number and ν is the vibrational frequency. The vibrational frequency represented by the harmonic oscillator model is

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$

where k is the force constant and μ is the reduced mass.

For molecule CX, where X is an unknown atom on the periodic table, the vibrational absorption energy from the vibrational ground state to the first vibrational excited state is 2170.0 cm^{-1} and the force constant is $1.903 \times 10^3 \text{ kg s}^{-2}$.

4.1 Find the reduced mass of CX in amu.

4.2 What is atom X.

3 POTD 3: More Harmonic Oscillator

This is problem 6 of the 2018 IChO Preparatory Problems

Various isotopes of a given atom obey the same chemical principles, but their different masses cause different behaviour in a dynamic sense. The kinetic isotope effect refers to a phenomenon wherein isotopically substituted molecules react at different rates. It was postulated in 1933 by Eyring and Polanyi and since then kinetic isotope effects have provided detailed information about mechanisms of many organic and biochemical reactions.

Vibrational modes are quantized and we can use the harmonic oscillator approximation for the description of the stretching modes. The energy level E_v can be calculated as:

$$E_v = \left(v + \frac{1}{2} \right) h\nu$$

where $v = 0, 1, 2, \dots$ is the vibrational quantum number and ν the frequency which depends on the force constant k and the reduced mass μ :

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$

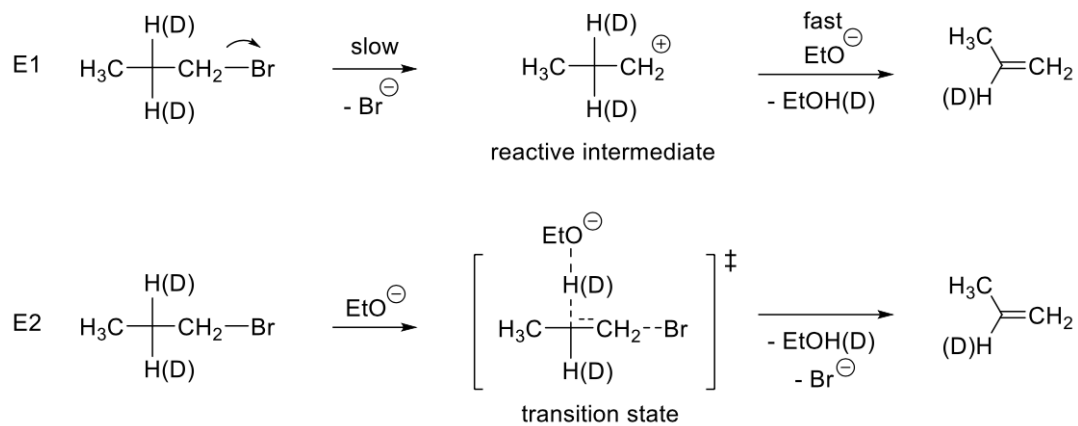
Note for the following calculations: unless stated otherwise, round the isotopic mass in amu to the nearest integer.

6.1 Let us start with a simple diatomic molecule ^1HF . Calculate its harmonic vibrational wavenumber in cm^{-1} and energies of the first two vibrational levels in J. The value of the harmonic force constant is $k = 968 \text{ kg s}^{-2}$.

6.2 Isotopic substitution does not change the potential energy surface of a molecule. Therefore, k remains unaffected. Given the vibrational wavenumbers of $^1\text{H}^{\text{A}}\text{X}$ (2439.0 cm^{-1}) and $^2\text{D}^{\text{A}+2}\text{X}$ (1734.8 cm^{-1}), determine the unknown element X.

6.3 Zero-point vibrational energy is the key contributor to the kinetic isotope effect. If we assume that the bond is fully broken at the transition state and only the ground vibrational state is populated, the difference in activation energies has the same absolute value as the difference in zero-point vibrational energies. The wave numbers of the C–H and C–D are 2900 cm^{-1} and 2100 cm^{-1} respectively. Calculate the ratio of the rate constants $k(\text{C–H})/k(\text{C–D})$ for the cleavage of the C–H/D bond at 300K taking into account only the difference in zero-point vibrational energies.

6.4 Kinetic isotope effects provide insight into the rate-determining step of a reaction mechanism. The ratio of $k_{\text{H}}/k_{\text{D}}$ for the formation of propene from 1-bromopropane and 1-bromo-2,2-dideuteriopropene in basic solution is 6.5. Does the reaction proceed by E1 or E2 mechanism? E1 takes place in two steps: formation of the carbocation intermediate followed by loss of H^+ . E2 occurs in a single step involving removal of the halide at the same time as the neighbouring hydrogen.



6.5 Let us consider the formation of the corresponding alkene from 2-bromo-3,3-dideuterio-2-methylbutane and its light-hydrogen analogue upon heating in ethanol. How significant would the kinetic isotope effect be in this case?

4 POTD 4: KIEs and ZPEs!

This is problem 2 of 2017 IChO

The kinetic isotope effect (KIE) is a phenomenon associated with a change in rate constant of the reaction when one of the atoms is replaced by its isotope. KIE can be used to confirm whether a particular bond to hydrogen is broken in the reaction. The harmonic oscillator model is used to estimate the difference in the rate between C-H and C-D bond activation ($D = \frac{1}{2}H$).

The vibrational frequency (ν) represented by harmonic oscillator model is

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$

where k is the force constant and μ is the reduced mass.

The vibrational energies of the molecule are given by

$$E_n = \left(n + \frac{1}{2} \right) h\nu$$

where n is vibrational quantum number with possible values of 0, 1, 2, ... The energy of the lowest vibrational energy level (E_n at $n = 0$) is called **zero-point vibrational energy (ZPE)**.

2-A1) Calculate the reduced mass of C-H (μ_{CH}) and C-D (μ_{CD}) in atomic mass unit. Assume that the mass of deuterium is twice that of hydrogen.

If students are unable to calculate the values for μ_{CH} and μ_{CD} in **2-A1)**, use $\mu_{CH} = 1.008$ and $\mu_{CD} = 2.016$ for the subsequent parts of the question.

2-A2) Given that the force constant (k) for C-H stretching is the same as that for the C-D stretching and the C-H stretching frequency is 2900 cm^{-1} , find the corresponding C-D stretching frequency (in cm^{-1}).

2-A3) According to the C-H and C-D stretching frequencies in question **2-A2)**, calculate the zero-point vibrational energies (ZPE) of C-H and C-D stretching in kJ mol^{-1} .

If students are unable to calculate the values for ZPE in 2-A3), use $ZPE_{CH} = 7.23 \text{ kJ/mol}$ and $ZPE_{CD} = 2.15 \text{ kJ/mol}$ for the subsequent parts of the question. Note that the given values are not necessarily close to the correct values.

Kinetic isotope effect (KIE)

Due to the difference in zero-point vibrational energies, a protonated compound and its corresponding deuterated compounds are expected to react at different rates.

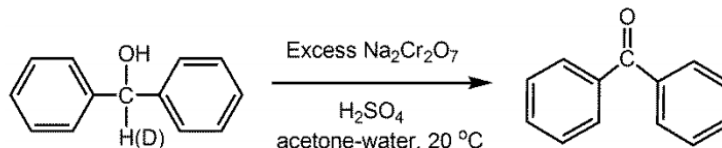
For the C-H and C-D bond dissociation reactions, the energies of both transition states and both products are identical. Then, the isotope effect is controlled by the difference in the ZPE's of the C-H and C-D bonds.

2-A4) Calculate the difference in the bond dissociation energy (BDE) between C-D bond and C-H bond ($BDE_{CD} - BDE_{CH}$) in kJ mol^{-1} .

2-A5) Assume that the activation energy (E_a) for the C-H/C-D bond cleavage is approximately equal to the bond dissociation energy and the Arrhenius factor is the same for both C-H and C-D bond cleavage. Find the relative rate constant for the C-H/C-D bond cleavage (k_{CH}/k_{CD}) at 25°C .

Using KIE to study reaction mechanism

The oxidation of nondeuterated and deuterated diphenylmethanol using an excess of chromic acid was studied.



Let C_0 be the initial concentration of either nondeuterated diphenylmethanol or deuterated diphenylmethanol and C_t its concentration at time t . The experiment led to two plots (Figure 2a and Figure 2b), from which the first-order rate constant can be determined.

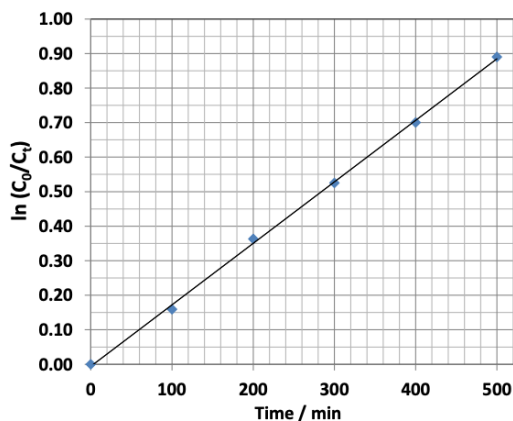


Figure 2a

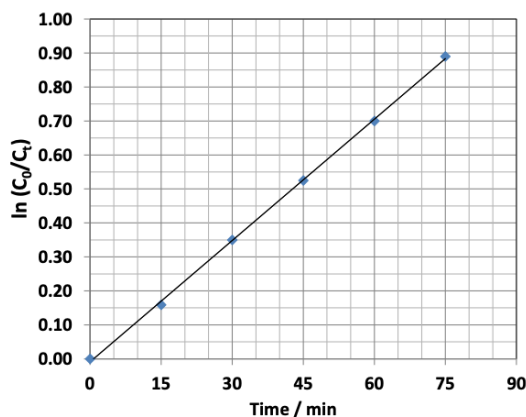


Figure 2b

2-A6) Which plot should be for the oxidation of nondeuterated diphenylmethanol and which one is for the oxidation of deuterated diphenylmethanol?

5 POTD 5-7: Georgia Iodine

The following POTDs are from various parts of problem 3 of 2016 IChO

POTD 5

Iodine deficiency is of special concern in Georgia because it occupies a region where iodine is scarce in soil and water. Iodine deficiency can be effectively and inexpensively prevented if salt for human consumption is fortified with small amounts of iodine. Methods for analyzing salt for iodine content are thus important. Current regulations in Georgia are that iodized salt must contain between 25-55 ppm iodine (1 ppm = 1 mg iodine/kg salt).

Most salt is iodized by fortification with potassium iodate (KIO_3). Iodate content can be determined in salt samples using iodometric titration. In a typical procedure, 10.000 g of an iodized salt sample is dissolved in 100 cm^3 of 1.0 mol/dm^3 aqueous HCl to which 1.0 g KI has been added. The solution is then titrated with 0.00235 mol/dm^3 aqueous sodium thiosulfate solution to a starch endpoint; this requires 7.50 cm^3 of titrant.

3.1.1. Write a balanced net ionic equation for the reaction when iodate reacts with excess iodide in acidic solution.

3.1.2. Write a balanced net ionic equation for the reaction taking place during the titration with thiosulfate.

3.1.3. Calculate the iodization level, in ppm, of this salt sample.

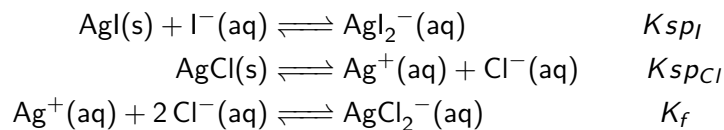
POTD 6

A less common agent for iodizing salt is potassium iodide, which cannot be easily measured by iodometric titration.

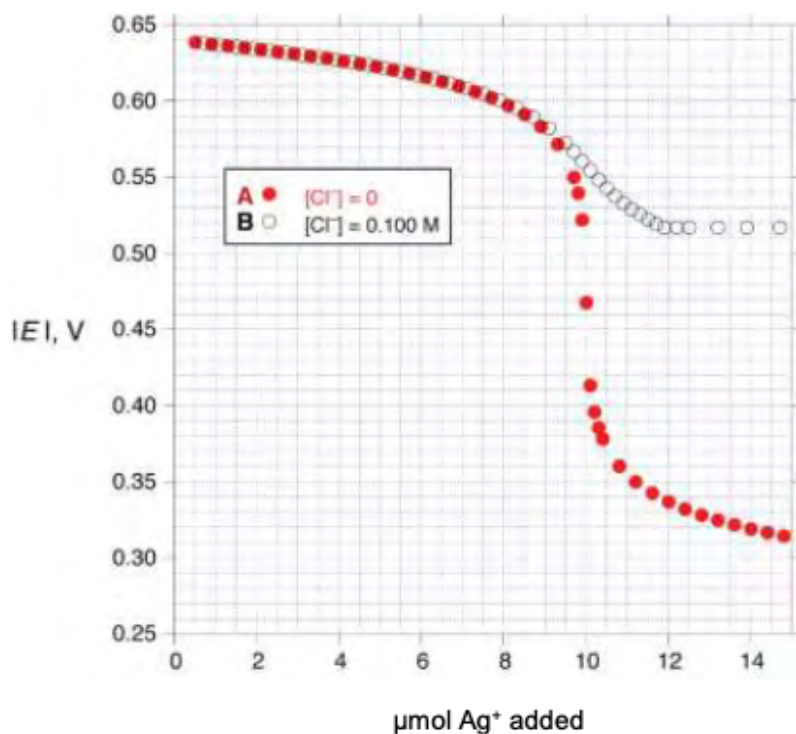
One possible method for analyzing iodide in the presence of chloride is potentiometric titration. However, this method is not very precise in the presence of large amounts of chloride.

In this method, a silver wire is immersed in the solution (containing iodide and chloride) to be analyzed and silver ion is gradually added to the solution. The potential of the silver wire is measured relative to a reference electrode consisting of a silver wire in a 1.000 mol/dm^3 solution of AgNO_3 . The measured potentials are negative and the absolute values of these potentials are reported. The solution to be analyzed has a volume of 1.000 dm^3 (which you may assume does not change as silver ion is added), and $T = 25.0\text{ }^\circ\text{C}$.

The results of this experiment are governed by three equilibria: the solubility of AgI(s) [$K_{sp\text{I}}$] and AgCl(s) [$K_{sp\text{Cl}}$] and the formation of $\text{AgCl}_2^-(\text{aq})$ [K_f]. (Iodide also forms complex ions with silver but this may be neglected at the very low concentrations of iodide present in this experiment).



Below are shown the results of two experiments measuring the observed potential as a function of added number of moles of silver ion. Experiment **A** (solid circles) was carried out with 1.000 dm³ of solution containing 1.00 · 10⁻⁵ mol/dm³ iodide and no chloride ion. Experiment **B** (open circles) was done using 1.000 dm³ of solution containing 1.00 · 10⁻⁵ mol/dm³ iodide and 1.00 · 10⁻¹ mol/dm³ chloride.



μmol Ag ⁺ added	E , V exp. A	E , V exp. B
1.00	0.637	0.637
3.00	0.631	0.631
5.00	0.622	0.622
7.00	0.609	0.610
9.00	0.581	0.584
10.0	0.468	0.558
11.0	0.355	0.531
12.0	0.337	0.517
13.0	0.327	0.517
15.0	0.313	0.517

3.2.1. Select an appropriate data point from the experiments and use it to calculate the solubility product of AgI (K_{spI}).

3.2.2. Select an appropriate data point from the experiments and use it to calculate the solubility product of AgCl (K_{spCl}).

3.2.3. Select an appropriate data point from the experiments and use it to calculate K_f . You may need to use values of K_{spI} or K_{spCl} to do this calculation. If you were unable to carry out the calculations in **3.2.1.** or **3.2.2.**, you may use the arbitrary values of $K_{spI} = 1.00 \cdot 10^{-15}$ and $K_{spCl} = 1.00 \cdot 10^{-9}$ without penalty.

POTD 7

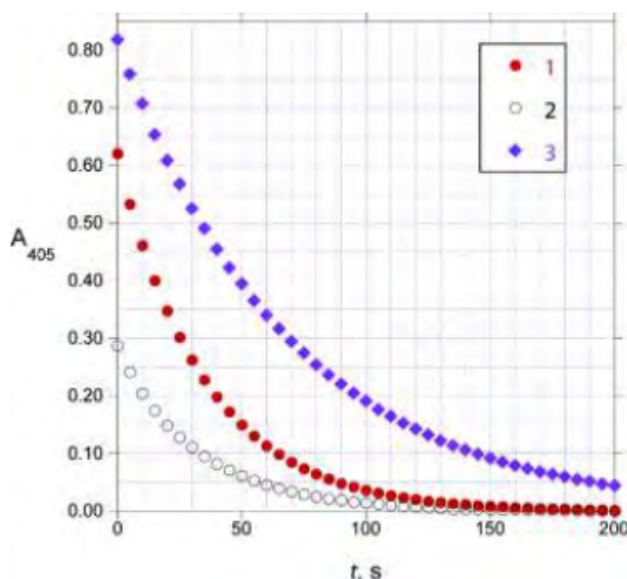
An analytical method that is more practical, because it is not sensitive to the presence of chloride, uses the Sandell-Kolthoff reaction. This is the reaction of H_3AsO_3 with Ce(IV) to give Ce(III) in acidic solution, which is strongly catalyzed by iodide ion.

3.3.1. Write balanced net ionic equations for the reaction of cerium(IV) with H_3AsO_3 in acidic solution, as well as reactions of cerium(IV) with a species containing the element iodine and H_3AsO_3 with a species containing the element iodine, that could reasonably account for the catalysis of the net reaction by iodide.

The reaction of Ce(IV) with H_3AsO_3 can be monitored by measuring the absorbance at 405 nm, as Ce(IV) is orange and absorbs significantly at 405 nm, while the other reactants and products are colorless and do not absorb appreciably. Three runs were carried out, all in $0.50 \text{ mol/dm}^3 \text{ H}_2\text{SO}_4$ at $25.0 \text{ }^\circ\text{C}$ using the following initial concentrations:

Run	$[\text{H}_3\text{AsO}_3]_0, \text{ mol/dm}^3$	$[\text{Ce(IV)}]_0, \text{ mol/dm}^3$	$[\text{I}^-]_0, \text{ mol/dm}^3$
1	0.01250	0.00120	$1.43 \cdot 10^{-6}$
2	0.00625	0.00060	$1.43 \cdot 10^{-6}$
3	0.01250	0.00120	$7.16 \cdot 10^{-7}$

An analyst initiated the reactions by mixing the reagents in a cuvette. After a short variable delay absorbance measurements were started, with the first measurement recorded at $t = 0 \text{ s}$. The data obtained are shown below:



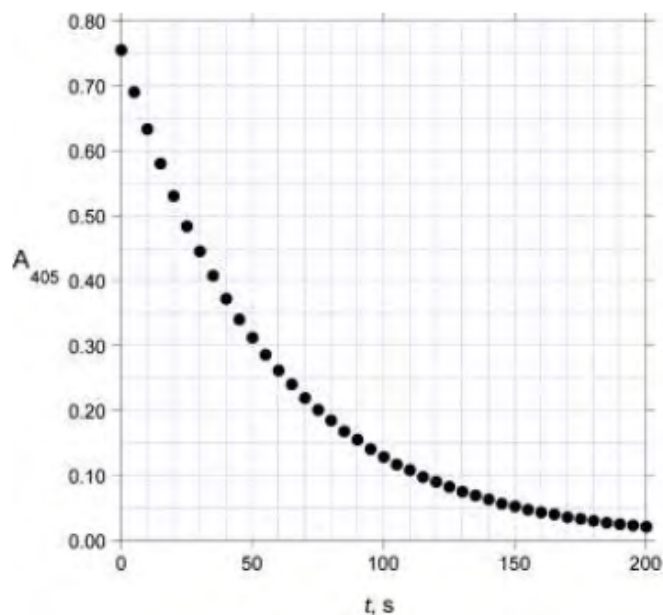
$t, \text{ s}$	A_{405} Run 1	A_{405} Run 2	A_{405} Run 3
0	0.621	0.287	0.818
20	0.348	0.149	0.608
40	0.198	0.083	0.455
60	0.113	0.046	0.340
80	0.064	0.025	0.254
100	0.037	0.014	0.191

Under these conditions ($0.5 \text{ mol/dm}^3 \text{ H}_2\text{SO}_4$, $25.0 \text{ }^\circ\text{C}$), the rate law for the reaction can be written as

$$\text{Rate} = k[\text{H}_3\text{AsO}_3]^m[\text{Ce(IV)}]^n[\text{I}^-]^p \text{ where } m, n, p \text{ are integers.}$$

3.3.2. Determine the values of m, n, p and calculate the value of k (be sure to specify its units).

A 1.000 g sample of iodized salt is dissolved in water to give 10.00 cm³ of solution. A 0.0500 cm³ aliquot of this solution is added to a mixture containing 1.000 cm³ of 0.025 mol/dm³ H₃AsO₃ in 0.5 mol/dm³ H₂SO₄ and 0.800 cm³ of 0.5 mol/dm³ H₂SO₄. To this mixture is added 0.200 cm³ of 0.0120 mol/dm³ Ce(NH₄)₂(NO₃)₆ in 0.5 mol/dm³ H₂SO₄ and the absorbance at 405 nm is measured as a function of time at 25.0 °C:



<i>t, s</i>	<i>A</i> ₄₀₅
0	0.756
20	0.531
40	0.373
60	0.262
80	0.185
100	0.129

3.3.3. Calculate the iodization level, in ppm, of this salt sample.

8 POTD 8: Chemical Dating

This problem was original (inspired by #1 of the 2009 Preparatory problems) and proposed by Thom-brom. You can find it on the discord server. If chemical dating is to be performed for old samples of various rocks with lifespans of several billions of years, radioactive methods are often performed. The following method is based on the radioactive decay of the Rubidium-87 isotope, which occurs by beta-radiation to become Strontium-87, a stable isotope. The following table consists of ratios of Rubidium-87 to Strontium-86 along with Strontium-87 to Strontium-86 ratios measured of lunar rock samples from the Apollo 11 mission.

Sample Nr.	Piece	$^{87}\text{Rb}/^{86}\text{Sr}$	$^{87}\text{Sr}/^{86}\text{Sr}$
10003, 20	Total	0.0114	0.69996
10062, 36	Total	0.0133	0.70003
10045, 20	Total	0.013	0.70005
10045, 20	Plagioclase	0.0129	0.69999
10045, 20	Pyroxene	0.022	0.70036
10047, 21	Total	0.0153	0.70009
10047, 21	Plagioclase	0.00268	0.69949

Table 1: Isotopic ratios of lunar rocks from Apollo 11. Source: Science Vol. 167, No. 3918 pp. 474-476

The formation of these rocks occur when liquid magma slowly cools and solidifies. In this process, Rubidium substitutes Potassium in the rocks crystal structure.

Strontium is a naturally occurring isotope, and thus the initial ratio of Strontium-87 to Strontium-86 can be assumed the same for all the rock samples. The half-life of Rubidium-87 has been measured to be $4.8 \cdot 10^{10}$ y.

- 1) Propose an equation for the number of Rubidium-87 at a time t based on the initial $N(^{87}\text{Rb})_0$ amount of Rubidium-87 atoms.

It can be assumed that the only way Strontium-87 is formed is by the decay of Rubidium-87.

- 2) Propose a relation between the ratio of $^{87}\text{Sr}/^{86}\text{Sr}$ based on the ratios $^{87}\text{Rb}/^{86}\text{Sr}$ and $^{87}\text{Sr}_0/^{86}\text{Sr}$, where the last ratio denotes the initial ratio at the time of magma-solidification.
- 3) Based on only the initial two samples in table 1, calculate the age of the moon.
- 4) Extend the above calculation to include the entire table of ratios.

9 POTD 9: Austrian Heat

This is problem 2 of the 2015 AusChO

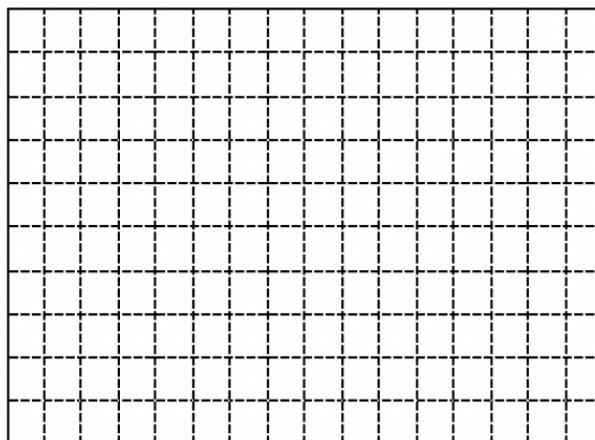
As a consequence of the second law of thermodynamics, the work performed by a periodically working piston will be smaller than the amount of heat that must be input.

Let us look at a thermodynamic cycle of a piston which contains 3.0 mol of argon. The cycle consists of the following four steps:

- $A \rightarrow B$: reversible isothermal expansion from p_A , $V_A(30.0 \text{ L})$ to $p_B(1.70 \text{ bar})$, V_B at $800 \text{ }^\circ\text{C}$
- $B \rightarrow C$: isochoric cooling to $235 \text{ }^\circ\text{C}$
- $C \rightarrow D$: reversible isothermal compression to V_A
- $D \rightarrow A$: isochoric heating

1. Calculate the efficiency of the machine.
2. Calculate the values of pressure and volume at points A , B , C , and D , and give a sketch of this thermodynamic cycle using the p-V-diagram below:

Shade in the portion which corresponds to the net-work of the system.



3. Calculate the work done by the reversible isothermal expansion at $800 \text{ }^\circ\text{C}$ in $A \rightarrow B$ and the heat which is released to the surrounding of the machine.

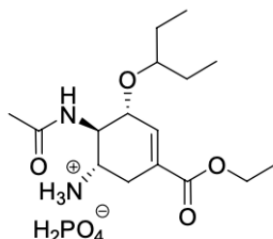
Consider instead the gas in the piston being reversibly and adiabatically expanded starting from point A until it reaches V_B .

4. Calculate the final temperature and the final pressure of this adiabatic expansion.
5. Compute the amount of work done in this expansion.

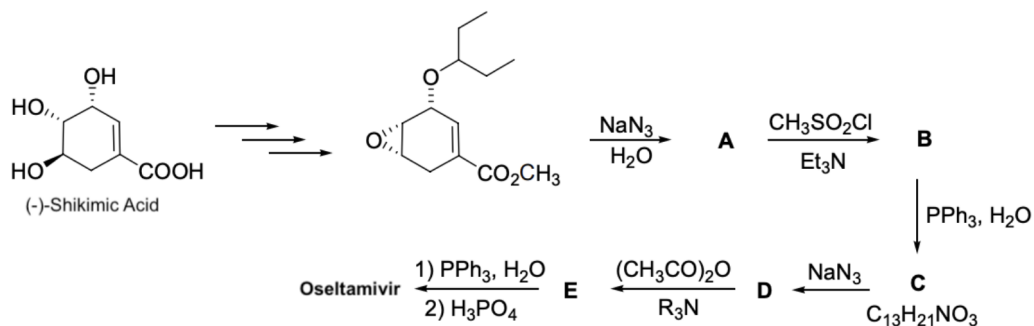
10 POTD 10: Tamiflu

This problem is taken from part of 2011 Russian National Chemistry Olympiad Tour 2 Task 1

In 2009, a swine flu pandemic swamped the world, the virus of which was resistant to exposure to commonly used M2 protein inhibitors such as rimantadine and amantadine in the treatment of conventional flu. Effective against swine flu are only compounds which inhibit the enzyme neuraminidase. The most popular drug of this type is Oseltamivir (trade name Tamiflu):



This drug was developed by Gilead Sciences Inc. Scientists of this company used natural (-)-shikimic acid as the starting material (a simplified synthesis scheme is given below):

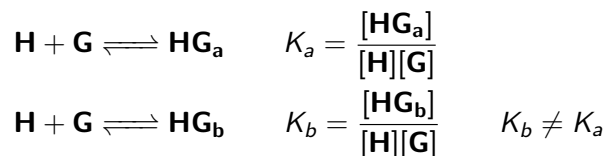


1. Write the structural formulas of compounds A – D, taking into account that the opening of the three-membered ring by nucleophiles can be considered as an example of the S_N2 reaction, that is, the attack by the nucleophile proceeds at the less hindered carbon atom, leading to inversion of configuration.

11 POTD 11: Molecular Cell Biology

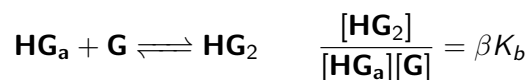
This is problem 3 of the 2015 IChO

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:



where **HG₂** is the completely bound complex.

1.1. 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);

1.2. Find the equilibrium constant for the process: $\mathbf{HG}_b + \mathbf{G} \rightleftharpoons \mathbf{HG}_2$ in terms of binding constant(s) and interaction factor

2.1. The solution was prepared with the initial concentrations $[\mathbf{H}]_0 = 1 \text{ M}$ and $[\mathbf{G}]_0 = 2 \text{ M}$. 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 .

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

2.2. Find the correct order of standard molar Gibbs energies of formation of host **H** and all hostguest complexes from **H** and **G**.

2.3. 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 **HG₂** 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 **2.1**.

2.4. 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**.

12 POTD 12: Basic particle in a box

This is problem 1 of the 2014 IChO

In quantum mechanics, the movement of π electrons along a neutral chain of conjugated carbon atoms may be modeled using the 'particle in a box' method. The energy of the π electrons is given by the following equation:

$$E_n = \frac{n^2 h^2}{8mL^2}$$

where n is the quantum number ($n = 1, 2, 3, \dots$), h is Planck's constant, m is the mass of electron, and L is the length of the box which may be approximated by $L = (k + 2) \times 1.40 \text{ \AA}$ (k being the number of conjugated double bonds along the carbon chain in the molecule). A photon with the appropriate wavelength λ may promote a π electron from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). An approximate semi-empirical formula based on this model which relates the wavelength λ , to the number of double bonds k and constant B is as follows:

$$\lambda(\text{nm}) = B \times \frac{(k + 2)^2}{(2k + 1)}$$

Part A Using this semi-empirical formula with $B = 65.01 \text{ nm}$ calculate the value of the wavelength λ (nm) for octatetraene ($\text{CH}_2 = \text{CH} - \text{CH} = \text{CH} - \text{CH} = \text{CH} - \text{CH} = \text{CH}_2$).

Part B Derive Equation 1 (an expression for the wavelength λ (nm) corresponding to the transfer of an electron from the HOMO to the LUMO) in terms of k and the fundamental constants, and hence calculate theoretical value of the constant B_{calc} .

Part C We wish to synthesize a linear polyene for which the excitation of a π electron from the HOMO to the LUMO requires an absorption wavelength of close to 600 nm. Using your expression from part **B**, determine the number of conjugated double bonds (k) in this polyene and give its structure.

[If you did not solve Part **B**, use the semi-empirical Equation 1 with $B = 65.01 \text{ nm}$].

Part D For the polyene molecule found in Part **C**, calculate the difference in energy between the HOMO and the LUMO, ΔE , ($\text{kJ} \cdot \text{mol}^{-1}$).

[In case Part **C** was not solved, take $k = 5$ to solve this problem.]

Part E The model for a particle in a one-dimensional box can be extended to a three dimensional rectangular box of dimensions L_x , L_y and L_z , yielding the following expression for the allowed energy levels:

$$E_{n_x, n_y, n_z} = \frac{h^2}{8m} \left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2} \right)$$

The three quantum numbers n_x , n_y , and n_z must be integer values and are independent of each other.

Give the expressions for the three different lowest energies, assuming that the box is cubic with a length of L .

Part F Levels with the same energy are said to be degenerate. Draw a sketch showing all the energy levels, including any degenerate levels, that correspond to quantum numbers having values of 1 or 2 for a cubic box.

13 POTD 13: More particle in a box

This is problem 1 of the 2020 CODS-CT Guide to USAPHO partner round

Bulk Sodium is highly conductive due to the small gap between the valence and conduction bands caused by delocalization. This conductivity can be modeled by the particle in a box model. It can be shown that the various energy levels for a particle such as an electron in a 1-dimensional box are given by:

$$E_n = \frac{n^2 h^2}{8mL^2} \quad n = 1, 2, 3, \dots$$

where m is the mass of the particle, L is the length of the box, and n is the energy level. Note that each energy level can be occupied by 2 electrons with opposite spins.

Consider a long chain of exactly $1 \cdot 10^5$ Sodium atoms in a straight line. Sodium has an atomic radius of 227 pm. Assume that the electrons are free to move between, but not beyond, the nuclei of the left and rightmost Sodium atoms. The mass of an electron is $m_e = 9.1 \cdot 10^{-31}$ kg.

1.1 Determine the energy of the highest occupied energy level in joules.

1.2 Write an expression for the HOMO-LUMO energy gap of the system in terms of the quantum number for the highest occupied energy level and then numerically compute it.

The approximate thermal energy of a molecule in a system is given by $E = k_b T$, where $k_b = R/N_a$ is the Boltzmann constant.

1.3 Is there sufficient thermal energy at 100 K to excite an electron into a higher energy orbital? Explain with calculations.

The energies of a particle in a 2d box is somewhat more complicated. Now the overall energy state is defined by 2 quantum numbers n_x and n_y . The energy levels are given by:

$$E_{n_x, n_y} = \frac{h^2}{8m} \left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} \right) \quad n_x, n_y = 1, 2, 3, \dots$$

Consider now a square sheet of Sodium atoms, with $1 \cdot 10^5$ Sodium atoms per side. Again, the same boundary conditions hold: electrons are free to move between, but not beyond, the nuclei of the left and rightmost Sodium atoms.

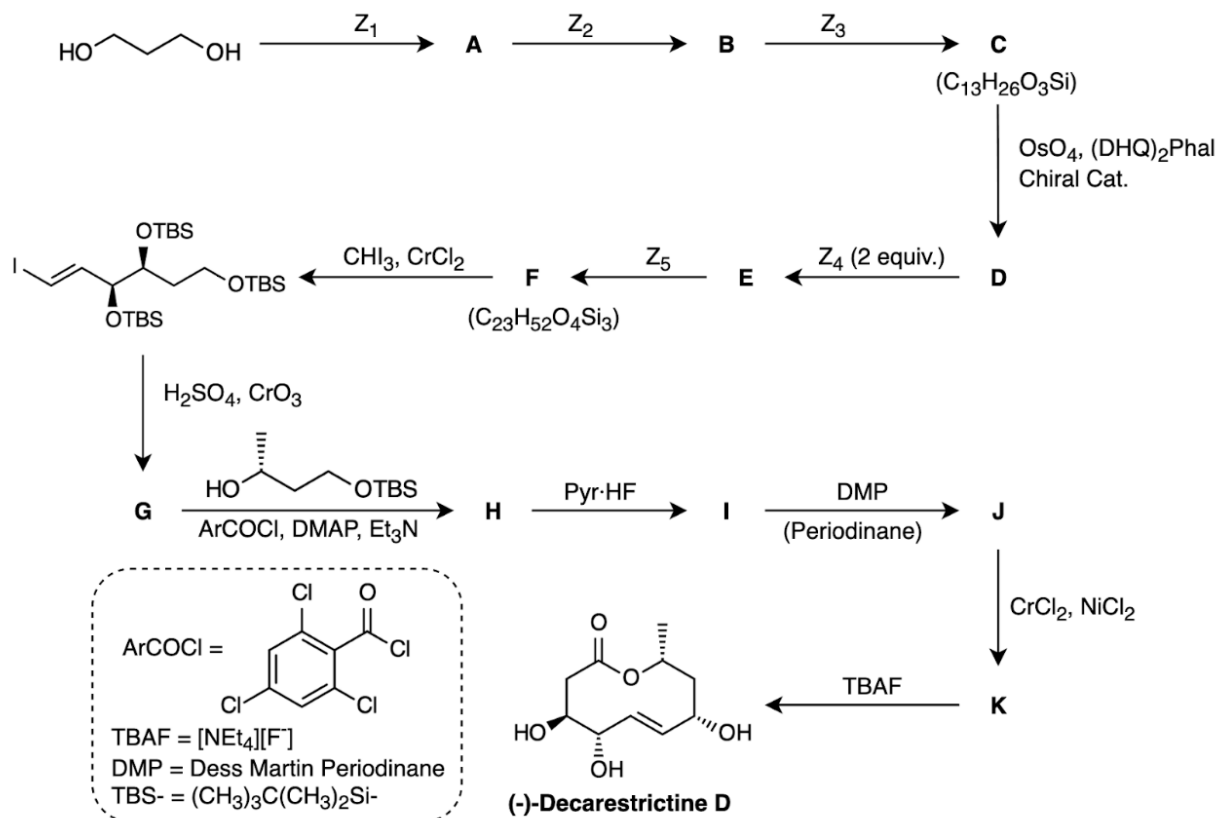
1.4 Approximate the energy of the highest occupied energy level in this system

1.5 Compute the total energy of all the valence electrons in this system according to the particle in a 2d box model.

14 POTD 14: Decarestrictine D

This problem is original

Consider the following synthesis of (-)-Decarestrictine D

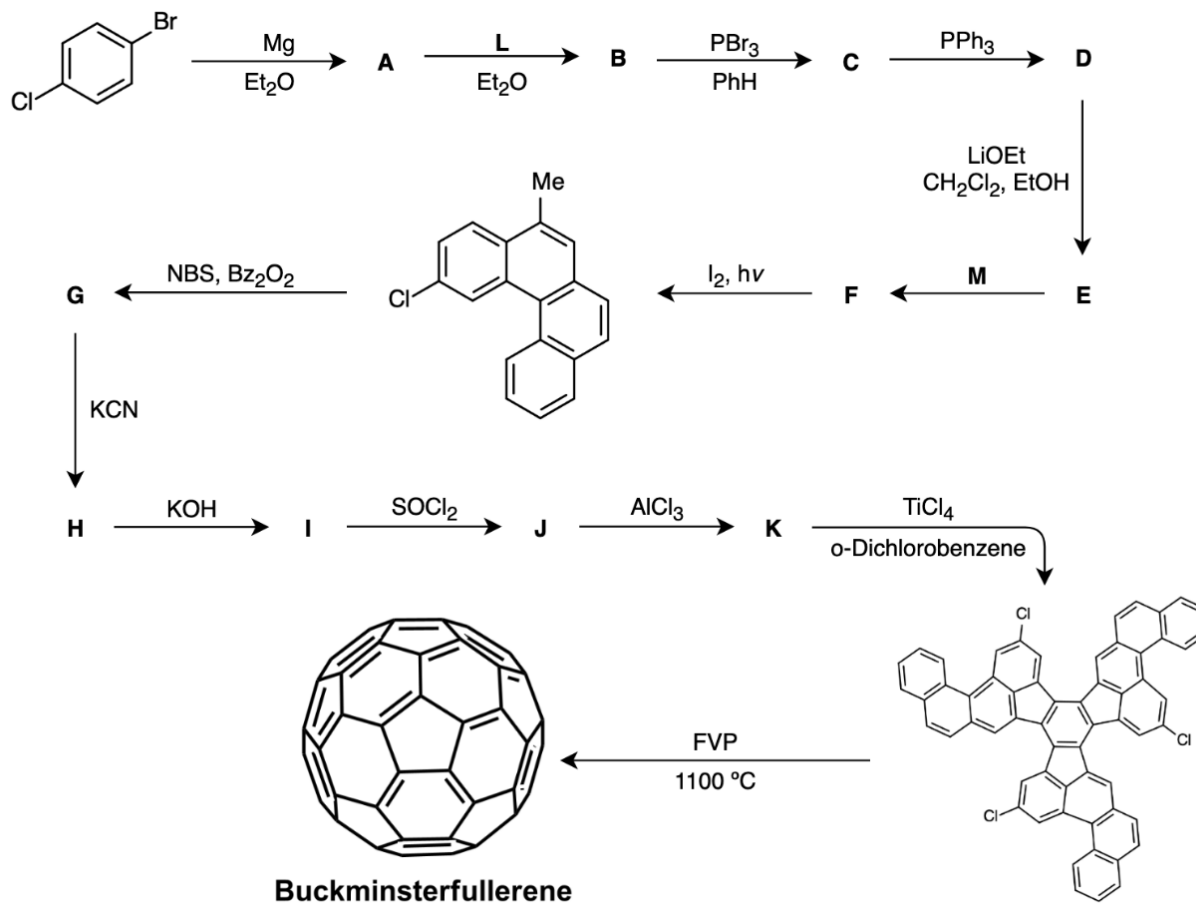


$\text{Z}_1 - \text{Z}_5$ are reagents/reaction conditions which you must propose.

1. Propose a suitable set of reagents $\text{Z}_1 - \text{Z}_5$ and the corresponding structures of **A-K**. More than one answer may be possible. You do not need to state solvents for $\text{Z}_1 - \text{Z}_5$.

15 POTD 15: Buckyballs

Buckminsterfullerene was synthesized in 2002 according to the following scheme



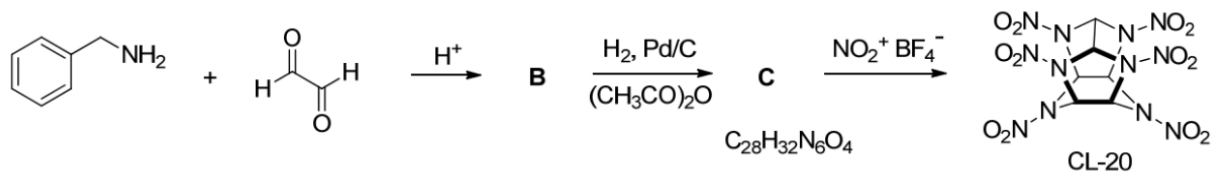
L and **M** are reactants which you must propose.

1. Draw the structures of intermediates **A** - **K** and propose reagents for **L** and **M**.

16 POTD 16: A quick organic puzzle

This problem is taken from part of 2012 Russian National Chemistry Olympiad Tour 2 Task 1

CL-20 is prepared as follows:



Draw **B** and **C**.

17 POTD 17: Pigments of Antiquity

This is problem 5 of 2016 IChO

5500 years ago in ancient Egypt people learned for the first time how to synthesize a blue pigment. Now we know this pigment as Egyptian blue. About 2000 years later in ancient China another pigment was widely used, which is now referred to as Chinese blue. The two pigments are similar in structure, but have different elemental compositions.



Ushabti figurines from Egyptian pharaoh tomb covered with Egyptian blue and a Chinese blue soap dispenser sold at Alibaba

The ancient method of preparation for these pigments can be easily reproduced in a modern laboratory. When considering the amounts, assume that all of the compounds in this task are pure, and the yields are quantitative.

To make **Egyptian blue**, one should heat 10.0 g of mineral **A** with 21.7 g of SiO_2 and 9.05 g of mineral **B** at $800 - 900^\circ\text{C}$ for a prolonged time. 16.7 dm^3 of a mixture of two gaseous products are released (the volume is measured at 850°C and $1.013 \cdot 10^5 \text{ Pa}$ (1.013 bar) pressure). In result, 34.0 g of the pigment was obtained. No other products are formed. As the gas mixture is cooled, one component of the mixture condenses. As the remaining gas is further cooled to 0°C , the gaseous volume reduces to 3.04 dm^3 .

5.1.1. Find the mass of the gaseous mixture formed upon heating of **A** with **B** and SiO_2 .

5.1.2. Determine the quantitative composition of this gas mixture.

When 10.0 g of mineral **A** is heated with 21.7 g of SiO_2 in the absence of **B**, it forms 8.34 dm^3 of gaseous products (measured at 850°C and $1.013 \cdot 10^5 \text{ Pa} = 1.013 \text{ bar}$ pressure). Mineral **A** contains only one metal.

5.1.3. Calculate the molar mass and determine the formula of mineral **B**. Hint: it is an ionic solid insoluble in water and containing no water of crystallization.

In order to obtain Chinese blue, one should take 17.8 g of mineral **C** instead of mineral **B** (keeping the amounts of mineral **A** and SiO_2 same as for Egyptian blue), and run the reaction at higher temperatures. Besides the pigment, the same gaseous products in the same quantities are formed as in the preparation of Egyptian blue.

5.1.4. Determine the formula of mineral **C**.

5.1.5. Determine the formulae of Egyptian blue and Chinese blue.

5.1.6. Determine the formula of mineral **A**.

Elemental analysis of some samples of Chinese blue shows traces of sulfur. This led to a conclusion that those were synthesized using another common mineral instead of **C**.

5.2.1. Suggest a formula for the mineral used in place of **C**.

5.2.2. Could the temperature of synthesis of Chinese blue be decreased if this mineral is used instead of **C**?

If during the synthesis of Chinese blue we take a smaller amount of silica than in the process above, we will obtain a purple pigment: Chinese violet. It was used, in particular, for coloring the famous Terracotta army soldiers.



Terracotta army from Xian, China and reconstruction of its original coloring

5.3. Write down the formula of a binary compound that forms under the conditions required for Chinese violet and is responsible for the change of the color.