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自動的に生成された説明

Preparatory Problems

Solutions and Comments

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Preface

We are very pleased to introduce the Preparatory Problems for the 53rd International Chemistry Olympiad. These problems cover a wide range of challenging and important topics in modern chemistry. We hope that both students and their mentors will enjoy solving these problems and prepare for the Olympics. The problems include 6 topics of advanced difficulty for the Theoretical part and 3 topics of advanced difficulty for the Practical part, in addition to the subjects normally covered in high school chemistry courses. These topics are explicitly listed under "Fields of Advanced Difficulty" and their applications are shown in the preparatory problems consisting of 31 theoretical problems and 6 practical tasks. The solutions will be emailed to the head mentor of each country by February, 2021 and will be published online in July, 2021. We welcome any comments, corrections and questions about the problems via email to:

preparatory@icho2021.org.

The International Chemistry Olympiad is a great opportunity for young people from all over the world to deepen their understanding of the wonders of chemistry, and inspire each other. At the same time, it is a wonderful opportunity to make friends around the world, and enjoy the history and culture of the host country. COVID-19 is widespread all over the world and the situation is very severe, but we hope that we can meet you in Osaka, Japan in July.

Acknowledgement

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Problem 1. Revision of SI unit

1-1.

 *n* = 8

1-2.  is modified to give:

 kg m-3

1-3. Combining the relationships  and  yields:

 *N*A = 6.04 × 1023

2-1. As the Avogadro and Planck constants are dependent on each other, having the Planck constant is the same as having the Avogadro constant.

■alone is sufficient □both  and *h* are required ■*h* alone is sufficient

2-2. As the Planck constant is:

*h* = 6.62607015 × 10-34 kg m2 s-1 = 6.62607015 × 10-34 × 1 kg (1 m)2 (1 s)-1,

we obtain:



2-3. Given that the wavelength is correlated to the frequency according to , mass can be calculated by:

 kg

Problem 2. Does water boil or evaporate?

1. When 1 mol of liquid water evaporates to water vapor at [bar] the entropy change is . The entropy of the water vapor at [bar] is by larger than that at . Therefore, when 1 mol of liquid water evaporates to water vapor at , the change in entropy can be derived from as:
2. The boiling point corresponds to the temperature where the Gibbs energy change is 0 when liquid water evaporates to water vapor at 1 bar.

From:

follows that:

1. The saturated vapor pressure at a given temperature is the pressure where the Gibbs energy change is 0 when water evaporates at that temperature. The Gibbs energy change when water is evaporated at a pressure and temperature can be derived from as

When is equal to the saturated vapor pressure:

then:

From = 1 bar, it follows that:

1. The Gibbs energy change when 1 mol of liquid water evaporates at of water vapor can be derived from as:

For =1 bar, it follows that:

1. Before moving the piston, the partial pressure of water vapor is , the partial pressure of Ar is , and the volume of gas is:

Let be the number of moles of water vapor:

Therefore, the number of moles of liquid water is:

When the piston is pulled back quickly and the volume is increased to 15.8 L, the partial pressures of water and Ar decrease to:

Here, as a realistic non-equilibrium state, it is assumed that the speed with which the piston is pulled back is sufficiently fast with respect to the speed with which water vaporizes.

Since the total pressure (0.5 bar) is smaller than the saturated vapor pressure of water the water begins to boil. The boiling stops when the total pressure (partial pressure of Ar + partial pressure of water vapor) becomes equal to the saturated vapor pressure of water at:

Let be the number of moles of water vapor:

Therefore, the number of moles of liquid water is:

After this point, evaporation proceeds until equilibrium is reached, i.e., when the partial pressure of water vapor reaches the saturation value of. Therefore:

Therefore, the number of moles of liquid water is:

Problem 3. Molecules meet water and metals

1-1. The density of seawater is 1.02 [g cm-3] = 1.02 10-3 [kg cm-3] 106 [cm3 m-3] = 1.02 103 [kg m-3]. The mass of a seawater column with a height of 20 m and a horizontal area of 1 m2 is 1 20 [m] 1.02 103 [kg m-3] = 2.04 104 [kg m-2]. Thus, the pressure exerted by this seawater column on the 1 m2 bottom surface is 2.04 104 N m-2 [= Pa] = 2.00 bar. Adding the atmospheric pressure of 1.01 bar to this pressure, we obtain a total pressure of 3.01 bar.

1-2. According to Henry's law, the mole fraction of nitrogen dissolved at 3.00 bar is 3.00/(8.57 104)= 3.50 10-5. The amount of water molecules in 5 L of water is 5 [kg]/18 [g mol-1] = 0.278 103 mol. Thus, the amount of dissolved nitrogen is 0.278 103 3.50 10-5 = 9.73 10-3 mol.

1-3. The amount of nitrogen dissolved in water at = 0.800 bar is 0.8/(8.57 mol. Thus, the volume of nitrogen gas is = (9.73 10-3 − 2.60 10-3) 8.31 298.15 /(0.8 105) = 2.21 10-4 m3 = 0.221 [L].

2-1. Let [mol] be the amount of CO2 molecules dissolved in the water, [mol] be amount of CO2 molecules in the gas phase, and [mol] be the amount of water molecules.

The mole fraction of CO2 can be estimated as because .

We thus obtain the following equations:

According to Henry’s law, = *k*H*/*;thus*,*  (1).

From the equation of the state of the gaseous part, :

(2)

The equation of the state for the gas initially added to the container:

(3)

Conservation of the amount of CO2 at the initial and equilibrated conditions gives:

(4)

Substituting equations (1)–(3) into equation (4) furnishes:

,

where

.

Thus, = 5.07 atm and = 0.135 mol.

2-2. The volume of CO2 dissolved in 0.5 L of water at 0 °C under 1 atm is V = 0.135 × 0.08201 × 273.15 / 1.0 = 3.03 L. Thus, 6.06 L of CO2 is dissolved in 1 L of water. Therefore, this solution is 6 GV carbonated water.

2-3. Following the same procedure as in Q2-1, we obtain = 12.1 atm and mol at 50C.

3-1. Using similar equations to those for Q2-1 with respect to oxygen at its partial pressure of 0.21 bar, the mole fraction of dissolved oxygen is calculated to be 4.8 10-6 and the mass is 8.4 mg.

1. Let be the quantities (*M*) after replacing the atmosphere with pure argon *j* times.   
   The equation of the state for the gas phase part affords*:*Henry's law for each gas:where are the amount of chemical species iin the gas phase and in water, respectively, while is the amount of water and  .   
   Conservation of the amount of oxygen before Ar replacement(*j* = 0) gives*:*  , where mol.After the first Ar replacement (*j* = 1): leads to and ,   
   where .   
   Because the oxygen dissolved in water before the replacement is distributed between the gas phase and water after the replacement, we obtain the relationship:  
      
   leading to [bar]. Thus, the oxygen dissolved in the water after the Ar replacement is:  
    [mol], where   
   Consequently: .
2. As found in Q3-2, the mole fraction of oxygen decreases by a factor of *g* with each argon replacement. Here, . Thus, the mole fraction of oxygen is (after the second substitution), (3rd), (4th), (5th). Therefore, 5 replacements are required to reduce the dissolved oxygen to 1 ppt or less.
3. The amounts of A and B are conserved before and after equilibrium:   
    (1)  
    (2)  
   The equations of state for the gases give:   
    , (3)  
    (4), where .   
   According to Henry’s law,   
    (5)  
   where (i = A, B).  
   From , , (6)  
   where is the amount of water.  
   Substituting equations (3)–(6) into equations (1) and (2), we obtain:  
    (7)  
    (8)  
   Solving the simultaneous equations with respect to *P*A and *P*B, we obtain:   
    [bar],   
    = 1.75 10-4, = 9.30 10-5.
4. Similarly, the mole fraction of B is calculated to be = 9.10 10-5 at bar and bar. Thus, this is 97.8% of the mole fraction of B in Q4-1.

5-1. Adsorption rate : , desorption rate:

5-2. Because at equilibrium:  
 .

Thus:

Dividing each side of the equation by and using and , we obtain:

5-3. Solving the above equation for *P,* we obtain:  
 .   
In the case of , *P* can be approximated as:  
.

5-4. The total amount of gas molecules introduced into the container is given as:  
   
At equilibrium, the number of molecules in the gas phase () and the number of molecules adsorbed on the metal surface () are and , respectively.  
As the total number of molecules is conserved before and after equilibrium:  
   
From these equations, we obtain = 58.7 Pa and = 0.998.

6-1. Similarly to Q5, we obtain:

Using , we obtain:  
 (1)  
 (2)

6-2. Using expressions (1) and (2), we obtain = 0.538 and = 0.462.

6-3.

6-4. When = 60.0 Pa, = 0.368, thus, it is 68.4% of the coverage at = 30.0 Pa.

Problem 4. Synthesis of diamonds

1.

|  |  |
| --- | --- |
| C(graphite) + O2 → CO2 | (graphite) = −393.5 kJ mol−1 |
| C(diamond) + O2 → CO2 | (diamond) = −395.3 kJ mol−1 |

Therefore,

|  |  |
| --- | --- |
| C(graphite) → C(diamond) | kJ mol−1 |

For the reaction above, the change in entropy is J K−1 mol−1.

kJ mol–1

|  |  |
| --- | --- |
| C60+ O2 → CO2 | kJ mol−1 |

Therefore,

|  |  |
| --- | --- |
| C(graphite) → C60 | kJ mol−1 |

For the reaction above, the change in entropy is J K−1 mol−1.

kJ mol–1

The order of stability is thus graphite > diamond > C60.

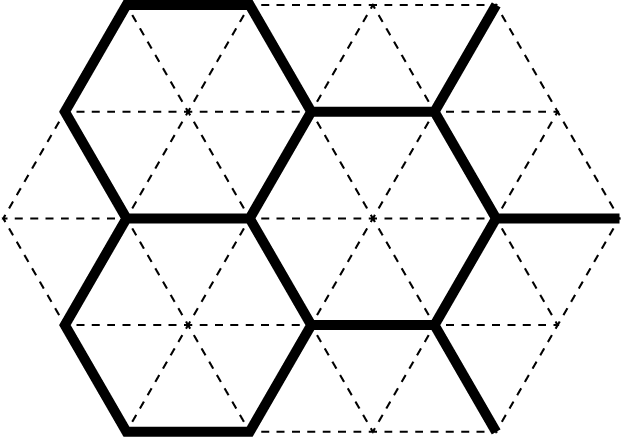
2. The reaction rate is very slow due to the high activation energy.

3.

|  |  |
| --- | --- |
| Cathode: | 2 C(diamond) + CaF2 + 2 e− → CaC2 + 2 F− |
| Anode: | 2 F− + CaC2 → 2 C(graphite) + CaF2 + 2 e− |

4. The change in Gibbs free energy of the conversion reaction from diamond to graphite is (*n* is the number of moles of electrons transferred per 1 mole of carbon, which is *n* = 1 in this case). The thermodynamic quantities for the conversion reaction of graphite to diamond are obtained by changing the sign. By comparing the result with , the enthalpy and entropy are found to be kJ mol−1 and J K−1 mol−1.

5.

　建物, 屋内, 座る, 天井 が含まれている画像

自動的に生成された説明　建物, 屋内, 座る, 天井 が含まれている画像

自動的に生成された説明

6. Left: 3R, center: 2H, right: 1H.

7. Left: lonsdaleite, right: diamond.

8. The area of the hexagonal cell that constitutes graphene is Å2.   
The number of carbon atoms within this hexagonal cell is two.  
Based on these values, the volume occupied by two carbon atoms can be calculated as Å3.  
Therefore, the density of graphite is 2.27 g cm−3.  
  
The side length of the unit cell of a diamond is times the distance between covalently bonded carbon atoms, which can be calculated to be 3.56 Å.  
There are eight carbon atoms in the unit cell.  
Based on these values, the volume occupied by eight carbon atoms can be calculated as Å3.  
Therefore, the density of diamond is 3.55 g cm−3.

9. If there is no volume change between graphite and diamond, the density of graphite and diamond should be the same. Using the results of Problem 8, the distance between layers can be calculated as 2.14 Å.

The distance between graphene layers is estimated to be as large as 2.78 Å even under 30 GPa (300,000 bar). Therefore, the direct conversion method requires high temperature in addition to high pressure to accelerate the reaction.

10.

11.

Based on this result, the conditions that the reaction constants should satisfy is given by .

12. Let the growth rate of the diamond be . (From here on, we assume that *r* and *A* are non-dimensional normalized by the unit μm h−1.)

Substituting in the experimental results gives:

From these equations, the value 49.4 kJ mol−1 is obtained.

13. Let the etching rate of the diamond be :

Substituting in the experimental results gives:

From these equations, the values 8486 and 83.8 kJ mol−1 are obtained.

14. At 1000 °C, the condition is fulfilled.

From this equation, the value 330 is obtained.

The condition that must be satisfied can be expressed as follows:

By substituting in the calculated values above and calculating the left-hand side of the above equation with different *T* values, *T* = 900 °C is obtained.

Problem 5. Count the number of states

1.

Using the approximate formula:

we obtain . Similarly:

2. As the number of states is maximized when an equal number of molecules is present in each of the two chambers A and B, *n*\* = 5 and 50, *i.e.*, the arrangements (5,5) and (50,50) are most probable for *N* = 10 and *N* = 100, respectively.

Given that each molecule has two possible locations, i.e., in either of the two chambers, the total number of possible arrangements of *N* molecules is 2*N*. Thus, the probability of the occurrence of the arrangement (n, m) is given by *P*(n,m) = *W*(n,m)/2*N*. Consequently:

In the case of *N* = 10, only the arrangement (5,5) falls within the specified range. In the case of *N* = 100, the following 5 arrangements are within this range: (48,52), (49,51), (50,50), (51,49), (52,48).

The numbers of states for each arrangement are:

Thus, we obtain:

Therefore:

This indicates that the probability of finding a state in the given *n*\* range is larger for *N* = 100 than for *N* = 10.

3. Using the analogy of one molecule in the container:

when *n* moles of molecules are present in the container, where *N*A is the Avogadro constant. Thus:

4.

5. The temperature, number of molecules, and volume do not change from State 1 to State 2. Thus, the entropy of the system does not change.

6. According to the equation derived in question 3, the entropy changes upon the expansion of gases of a and β is given by:

The volume ratios can be replaced by the ratios of the amounts of gas molecules to give:

Thus:

7. As both chambers are filled with identical molecules of type a, we cannot distinguish whether a molecule was originally present in chamber A or B after mixing. Furthermore, because the pressure is kept constant, there is no entropy change associated with expansion. Therefore, the entropy does not change from State 1 to State 2.

8. Given that a H3CD molecule in a crystal has four different orientations, the molar residual entropy is given by:

9-1. Along the O–O axis of two adjacent oxygen atoms there are two stable positions for a hydrogen atom, and each water molecule possesses two hydrogen atoms. Thus, the number of configurations for the hydrogen atoms of one water molecule without the constraints of the ice rules is 22 = 4. Thus, the number of configurations for 1 mole of water is .

9-2.

9-3.

(H4O)2+ : *W* = 1

(H3O)+ : *W* = 4

(OH)– : *W* = 4

O2– : *W* = 1

Thus, the number of configurations satisfying the ice rules is 16 – 10 = 6.

9-4. The number of configurations satisfying the ice rules in an ice crystal with one mole of water can be calculated by:

Thus, the molar residual entropy is given by:

Problem 6. The path of chemical reactions

1.

ダイアグラム, 概略図

自動的に生成された説明

To summarize 1–3 items in the equation

テキスト, 手紙

自動的に生成された説明

Thus

ダイアグラム

中程度の精度で自動的に生成された説明

2. *k*S < *k*D and *R*S0 > *R*D0

3.

図形

中程度の精度で自動的に生成された説明

4.

■ For the harmonic oscillator approximation (Eq. 4) and the Morse potential approximation (Eq. 6), the equilibrium internuclear distance is the same.

■ In the region where *R* is long, the Morse potential approximation is lower in energy than the harmonic oscillator approximation.

□ In the region where *R* is short, the Morse potential approximation and the harmonic oscillator approximation coincide.

■ As *a* increases in the Morse potential approximation, the width of the well becomes narrower.

5. The position of the bottom should be explicitly shown at (x,y)=(1,2).

図形 が含まれている画像

自動的に生成された説明

6. The pathway is a single line along the lowest point of energy.

ダイアグラム, 概略図

自動的に生成された説明

7. The pathway is a single line, oscillating in a direction normal to the progress of the reaction (when the reaction goes the vertical direction, the oscillation occurs horizontally or vice versa). Details of the amplitude and phase are not so important, but the amplitude is the narrowest in the transition state.

図形

自動的に生成された説明

8. A: *R*CM, B: *R*CH, C: *R*CC, D: *R*HF

Problem 7. Molecular vibrations and infrared spectroscopy

1. Given that the spring constant is identical in both compounds,  can be calculated by:

 with a reduced mass of .

As the wavenumber, , is related to the frequency, , via  (*c*: velocity of light):

 is obtained (= 3953.8 cm-1).

Consequently, we can reach the conclusion:  2866 cm-1.

(*cf.* experimentally observed position: 2896 cm-1)

2.



3. When calculating the frequency in wavenumbers using , take care regarding the unit conversion, especially for cm-1.

 K

4. A bent structure as depicted below should be drawn, because the fluorine atom has three lone pairs with an sp3 configuration.

ダイアグラム

自動的に生成された説明 L. Andrews and G.L. Johnson, *J. Phys. Chem.* **88**, 425 (1984).

5. (2) *k* becomes smaller and *m* becomes larger, which results in a shift to a lower wavenumber.

6. The wavenumber, where a peak appears in an IR spectrum corresponds to the energy gap between the two levels, , which can directly be used as  in the Boltzmann factor.



At 12 K: 

At 25 °C: 

Problem 8. Quantum chemistry of aromatic molecules

1.

図形

中程度の精度で自動的に生成された説明

(d)

図形, 四角形

自動的に生成された説明

2. In anthracene, the resonance structure shows that the fraction of double-bond character for each of the bonds is *R*3 = 3/4, *R*1 = 1/2, and *R*2 = 1/4.

*R*D (1.34) < *R*3 (1.356) < *R*1(1.410) < *R*2 (1.430) < *R*S(1.53)

3. benzene: 3; naphthalene: 5; pyrrole: 3

4. (c)

5. (a), (c), (b)

Problem 9. Protic ionic liquids

1-1. 2 CH3OH ⇄ CH3OH2+ + CH3O−

1-2. [CH3OH2+] = [CH3O−] = (10−16.7)½ = 4 × 10−9 mol L−1

2-1.

2-2.

Based on the above equation and the numerical values provided:

3-1.

By using the approximation ,

From these equations:

3-2.

This equation can be rearranged into the following form (Gran’s plot):

By substituting in the numerical values, *K*s = 5.1 × 10−13 mol2 L−2 is obtained.

4-1. When pH = 9.27 (= p*K*a), *fa* = 0.50.

1/2 = 1 − exp(−0.50 *k′ t*)

By solving the equation for *t*: *t* = 28 s.

4-2. 1/3 = 1 − exp(−*fa k′* 500)

By solving the equation for *fa*: *fa* = 1.62 × 10−2.

By solving the equation for [H3O+]: [H3O+] = 3.26 × 10−8 and pH = 7.49.

[Note] Proof of eq. 12 (for mentors only, students do not have to calculate by themselves):

Note that .

5-1.

Let [HB] = *x*,

By solving the equation for *x*: *x* = 2.75 × 10−9 mol L−1.

5-2. [R1–NH2]0 is calculated to be 10.00 × 10−3 mol L−1.

By solving the equation for [R1–NH3+] with [HB] = 5.39 × 10−17 mol L−1,

[R1–NH3+] = 5.75 × 10−3 mol L−1 is obtained.

[R1–NH2] = 10.00 × 10−3 mol L−1 − [R1–NH3+] = 4.25 × 10−3 mol L−1.

By solving the equation for [CH+], [CH+] = 2.46 × 10−4 mol L−1.

[C] = 6.00 × 10−3 mol L−1 − [CH+] = 5.75 × 10−3 mol L−1.

The result shows that [C] = [R1–NH3+], which means that all the protons dissociated from CH+ are transferred to R1–NH2.

5-3. Solve the following simultaneous equations. Note that 2.00 × 10−3 mol L−1 of R1–NH2 is consumed by the reaction between R1–NH2 and R2–CO–NHS, which generates 2.00 × 10−3 mol L−1 of protons. Therefore, the total proton concentration becomes 6.00 × 10−3 (concentration of CH+/B− solution) + 2.00 × 10−3 = 8.00 × 10−3 mol L−1.

|  |  |  |
| --- | --- | --- |
|  |  | (20) |
|  |  | (21) |
|  |  | (22) |

By substituting eq. 22 into eq. 21, the following is obtained:

|  |  |  |
| --- | --- | --- |
|  |  | (23) |

By substituting eq. 23 into eq. 20, the following is obtained:

|  |  |  |
| --- | --- | --- |
|  |  | (24) |

By substituting eq. 24 into eq. 23, the following is obtained:

|  |  |  |
| --- | --- | --- |
|  |  | (25) |

By solving eq. 25, [R1–NH3+] = 6.96 × 10−3 mol L−1 is obtained.

[R1–NH2] = 8.00 × 10−3 mol L−1 − [R1–NH3+] = 1.04 × 10−3 mol L−1.

By substituting these values into eq. 20, [HB] = 2.65 × 10−16 mol L−1 is obtained.

By substituting these values into eq. 21, [CH+] = 1.04 × 10−3 mol L−1 is obtained.

[C] = 6.00 × 10−3 mol L−1 − [CH+] = 4.96 × 10−3 mol L−1.

The result shows that [R1–NH3+] = [C] + 2.00 × 10-3 mol L−1, which means that all the protons dissociated from CH+ and the protons generated by the reaction (2.00 × 10-3 mol L−1) are transferred to R1–NH2.

5-4. From eq. 18, [HB] = *K*aC [CH+] / [C]

(By rearranging the above equation, the Henderson–Hasselbalch equation is obtained:

pH = p*K*aC − log([CH+] / [C])

5-5. 1/3 = 1 − exp(−*fa k′* 2000)

By solving the equation for *fa*: *fa* = 0.253.

By solving the equation for [HB], [HB] = 1.173 × 10−16.

From the equation of Q5-4, [C] / [CH+] = 10.73 and [C] = 1.07 mol L−1 are obtained.

Problem 10. The Yamada universal indicator

1-1. At pH = 2.00, only the protonated form is present. At pH = 12.00, only the deprotonated form is present. For example, the molar absorption coefficient of the protonated form at 420 nm can be calculated using the absorbance at pH = 2.00 as follows:

*ε* (420 nm) ∙ 200 × 10−6 mol L−1 ∙ 1 cm = 1.74 → *ε* (420 nm) = 8.7 × 103 mol−1 L cm−1

The other molar absorption coefficients are calculated in a similar way (unit: mol−1 L cm−1).

|  |  |  |  |
| --- | --- | --- | --- |
| Wavelength | 420 nm | 501 nm | 520 nm |
| Protonated | 8.7 × 103 | 3.5 × 103 | 1.8 × 103 |
| Deprotonated | 3.0× 103 | 3.5 × 103 | 5.3 × 103 |

1-2. Let the concentration of the protonated form be *x* mol L−1 and let that of the deprotonated form be *y* mol L−1. Using the conditions given in the problem, the following two equations are obtained:

8.7 × 103 *x* + 3.0 × 103 *y* = 1.13

1.8 × 103 *x* + 5.3 × 103 *y* = 0.52

By solving these equations, the values *x* = 1.09 × 10−4 and *y* = 0.61 × 10−4 are obtained. From the definition of the acid dissociation constant of BTB:

10−7.1 = [H+] *y*/*x*, [H+] = 1.41 × 10−7 mol L−1 → pH = 6.85

1-3, 4.

The pH does not matter, because 501 nm corresponds to the isosbestic point of BTB. The concentration of the indicator of the solution used in Q1-2 is *x* + *y* = 1.70 × 10−4 mol L−1. Therefore, the absorbance at 501 nm before dilution is 0.595. After the five-fold dilution, the absorbance is 0.119.

2. As examples, let us focus on the absorbance values that are highlighted in the following table:

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
|  | Color | Wavelength [nm] | | | | | |
| 400 | 450 | 500 | 550 | 600 | 650 |
| pH = 1.0 | Red | 0.236 | 0.407 | 0.655 | 0.609 | 0.028 | 0.000 |
| (1) | Yellow | 0.323 | 0.455 | 0.460 | 0.352 | 0.018 | 0.002 |
| (2) | Green | 0.435 | 0.440 | 0.176 | 0.121 | 0.179 | 0.089 |
| (3) | Blue | 0.466 | 0.360 | 0.645 | 1.979 | 0.673 | 0.275 |
| pH = 12.0 | Purple | 0.490 | 0.384 | 0.793 | 2.498 | 0.701 | 0.276 |

The concentrations of the indicators in the final solutions are as follows (unit: mol L−1):

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Indicator | TB | MR | BTB | PP |
| Concentration | 3.572 × 10−6 | 1.547 × 10−5 | 2.669 × 10−5 | 1.047 × 10−4 |

(1) The pH of the solution is estimated to be 3–6 because the color of the solution is yellow. In this pH region, it is reasonable to assume that all the TB and PP exist as HA−. Most of the BTB will exist as HA−, although there may be a small amount of A2−. Therefore, it is only necessary to focus on the HA−/A2− ratio of MR. In principle, we can calculate this ratio using any wavelength. Because the molar absorption coefficients of the HA− and A2− forms of BTB are the same at 500 nm, we can ignore the HA−/A2− ratio of BTB by using the absorbance at 500 nm. The contributions to the absorbance of the solution at 500 nm from TB, BTB, and PP are as follows:

TB: *ε* (HA−, 500 nm) = 3000, concentration: 3.572 × 10−6 mol L−1 → Absorbance: 0.011

BTB: *ε* (500 nm) = 3500, concentration: 2.669 × 10−5 mol L−1 → Absorbance: 0.093

PP: *ε* (HA−, 500 nm) = 0, concentration: 1.047 × 10−4 mol L−1 → Absorbance: 0.000

From these results, the absorbance at 500 nm originating from MR can be calculated to be 0.460 – 0.011 – 0.093 = 0.356.

By considering the concentration of the protonated form of MR, [HA−]MR, and that of the deprotonated form, [A2−]MR, which is 1.547 × 10−5 mol L−1 – [A2−]MR, the following equation is obtained:

35000 [HA−]MR + 4000 (1.547 × 10−5 – [HA−]MR) = 0.356

By solving the above equation, the values [HA−]MR = 9.49 × 10−6 mol L−1 and [A2−]MR = 5.98 × 10−6 mol L−1 are obtained.

By substituting these results into the definition of the acid dissociation constant of MR:

10−5.1 = [H+] [A2−]MR / [HA−]MR → [H+] = 1.26 × 10−5 mol L−1, pH = 4.9

(2) The pH of the solution is estimated to be 6–8 because the color of the solution is green. In this pH region, it is reasonable to assume that all the PP exists as HA−. However, it is difficult to estimate the ratios of the protonated forms of the other indicators in this pH region. From Table 4, we can see that the absorbance at 650 nm is governed by the deprotonated form of BTB. Although the A2− form of TB also contributes to the absorption, this contribution will be negligible because the concentration of TB is one order of magnitude smaller than that of BTB.

The following equation is then obtained for the concentration of the protonated form of BTB, [HA−]BTB:

10000 [HA−]BTB = 0.089

By solving the above equation, the values [HA−]BTB = 1.78 × 10−5 mol L−1 and [A2−]BTB = 2.669 × 10−5 mol L−1 – [HA−]BTB = 8.9 × 10−6 mol L−1 are obtained.

By substituting these results into the definition of the acid dissociation constant of BTB:

10−7.1 = [H+] [A2−]BTB / [HA−]BTB → [H+] = 1.59 × 10−7 mol L−1, pH = 6.8

From this pH, the ratio of TB that exists in the form of A2− can be calculated to be 0.8%. This confirms that the absorption of the A2− form of TB at 650 nm is negligible.

(3) The pH of the solution is estimated to be 8–11 because the color of the solution is blue. Additionally, based on the significant increase of the absorbance at 500 nm originating from the A2− form of PP, the pH of the solution is estimated to be 10–11. In this pH region, it is reasonable to assume that all TB, MR, and BTB exist as A2−. Therefore, it is only necessary to focus on the HA−/A2− ratio of PP. Similar to the case of Q2-1, let us use the absorbance at 500 nm so that we can ignore the HA−/A2− ratio of BTB. The contributions to the absorbance of the solution at 500 nm from TB, MR, and BTB are as follows:

TB: *ε* (A2−, 500 nm) = 3500, concentration: 3.572 × 10−6 mol L−1 → Absorbance: 0.013

MR: *ε* (A2−, 500 nm) = 4000, concentration: 1.547 × 10−5 mol L−1 → Absorbance: 0.062

BTB: *ε* (500 nm) = 3500, concentration: 2.669 × 10−5 mol L−1 → Absorbance: 0.093

From these results, the absorbance at 500 nm originating from PP can be calculated to be 0.645 – 0.013 – 0.062 – 0.093 = 0.477.

The following equation is then obtained for the concentration of the deprotonated form of PP, [A2−]PP:

6000 [A2−]PP = 0.477

By solving the above equation, the values [A2−]PP = 7.95 × 10−5 mol L−1 and [HA−]PP = 1.047 × 10−4 mol L−1 – [A2−]PP = 2.52 × 10−5 mol L−1 are obtained.

By substituting these results into the definition of the acid dissociation constant of PP:

10−9.7 = [H+] [A2−] / [HA−] → [H+] = 6.32 × 10−11 mol L−1, pH = 10.2

Problem 11. Silver electroplating

1. Because and are significantly lower than the concentrations of the other three species, these two will be considered later.

The three highest concentrations are:

= 0.07 mM

= 0.74 mM

= 0.19 mM

The relative concentrations of and can be addressed with the following equation:

　 ()

Therefore, .

Putting the above information together gives:

　＞　　＞　　＞　　＞

The dissolved species with the highest concentration is 0.74 mM.

2.

[V]

3. At the upper limit of ,

At the lower limit,

(note: )

The range is thus .

4.

5. From , the HER equilibrium potential is:

2

6. From

Problem 12. How does CO2 in the atmosphere affect the pH value of seawater?

1.

is negligible because the solution becomes acidic, and is also negligible because . Therefore,

M

2. The total concentration of carbon dioxide-related species is:

Among these four concentrations, is negligible as in Q1. Moreover, can also be neglected based on the relationship . Therefore, it is sufficient to consider the quantity:

.

The relationship between these two concentrations is:

Using this relationship, we compare the ratio of the initial and final values of for the cases where .

(a) In the case of ,

Because this is more than double, the answer is (1).

(b) For ,

The answer is (3).

(The total concentration significantly increases on the higher pH side, whereas the change is small on the lower pH side.)

3. Using the relationship obtained in Q1,

(This is the behavior of a weak acid.)

4.

is negligible as in Q1. Moreover, because the is ~8, and are negligible. Therefore,

(This behavior is based on the Henderson–Hasselbalch equation, and the pH change is double that in the pure water case in Q3.)

5.

Similar to Q4, , , and are negligible.

By solving this quadratic equation for , we find pH = 8.05.

In the same way, with we find pH = 7.80.

(The pH shift is milder than due to the equilibrium although is still more negative than , the threshold for coral survival).

6. (Region A)

(Region B)

(Region C) 0

Region A .

7. .

Problem 13.  How to produce sulfuric acid and dilute it without explosion

1. Reaction 1: 2 CuFeS2 + 2 SiO2 + 4 O2 → Cu2S + 2 FeSiO3 + 3 SO2

Reaction 2: Cu2S + O2 → 2 Cu + SO2

2. When the reaction proceeds completely, 1 mol of Cu and 2 mol of SO2 can be obtained with respect to 1 mol of CuFeS2.

CuFeS2 = 183.527 g mol–1

When the reaction proceeds completely from 100 kg of CuFeS2,

Cu: 100×103 × (63.546 / 183.527) [g] = 3.46×104 [g] = 34.6 [kg]

SO2: 100×103 / 183.527 × 2 [mol] = 1.09×103 [mol]

will be obtained.

According to the equation *PV* = *nRT*, *V* = *nRT*/*P* = 1.09×103 [mol] × 8.3145 [J mol–1 K–1] × (273 + 25) [K] / 1.00×105 [Pa] = 27.0 [m3] = 2.70×104 [L]

Answer: 34.7 kg of Cu and 2.70×104 L of SO2 are obtained.

3. Based on the exothermic reaction 2 SO2 + O2 ⇄ 2 SO3 and according to Le Chatelier’s principle, the reaction is shifted toward the product side at low temperature and high pressure.

Answer: (2)

4. 2 SO2 + O2 ⇄ 2 SO3

Let the number of moles of sulfur trioxide after the reaction be *n*(SO3) = *n*. The number of moles of SO2 and O2 can then be calculated as *n*(SO2) = 7 – *n* and *n*(O2) = 3 – *n* / 2. Thus, the total number of moles of gas molecules in the reaction vessel is *n* + (7 – *n*) + (3 – *n* / 2) = 10 – *n* / 2 [mol].

According to the equation *PV* = *nRT*:

8.60×105 [Pa] × 50.0×10–3 [m3] = (10 – n / 2) [mol] × 8.3145 [J mol–1 K–1] × 623 [K]

*n* = 3.40 [mol]

Answer: 3.40 mol

5. 20 kg of 32% fuming sulfuric acid consist of:

SO3: 20×103 × 0.32 = 6.4×103 [g] = 6.4×103 / 80.07 = 79.9 [mol]

H2SO4: 20×103 × 0.68 = 13.6×103 [g] = 1.36×104 / 98.08 = 138.7 [mol].

1 kg of 60% sulfuric acid consists of:

H2SO4 = 600 / 98.08 = 6.12 [mol] and H2O = 400 / 18.02 = 22.2 [mol].

Let *x* [kg] equal the mass of 60% sulfuric acid required for the dilution:

79.9 + 138.7 + (6.12 × *x*) = (20.0 + *x*) × 103 × 0.98 / 98.08

*x* = 4.84，Answer: 4.8 kg

6. Let *x* [kg] equal the mass of water required for the dilution:

8.0×103 × 0.98 = (8.0 + *x*)×103 × 0.60 → *x* = 5.07. Thus, 5.07 kg of water are needed for the dilution.

Now, let *m*(98) equal the number of moles of water required for the dilution of 1 mol of H2SO4 to 98%:

*m*(98) = 0.111 [mol]

In this dilution process, the heat of dilution *Q*1[J] is calculated as follows:

Let *m*(60) equal the number of moles of water required to dilute 1 mol of H2SO4 to 60%:

*m*(60) = 3.63 mol

In this dilution process, the heat of dilution *Q*2 [J] is calculated as follows:

From the values shown above, the heat of dilution when 98% sulfuric acid containing 1 mol of H2SO4 is diluted to 60% sulfuric acid can be calculated as:

*Q*2 – *Q*1 = 45600 [J]

8.0 kg of 98% sulfuric acid contain 8.0×103 × 0.98 / 98 = 80.0 mol of H2SO4. Thus, the heat of dilution when 8.0 kg of 98% sulfuric acid is diluted from 98% to 60% is *Q* = 45600 × 80.0 = 3.65×106 [J].

Answer: 3.7×106 J

The produced heat *Q* [J] can raise the temperature of 10 kg of water (0 °C) by:

3.65×106 / (10.0×103 × 4.18) = 87.3

Answer：87 ºC

Problem 14. Hydrolysis of C vs Si and the electronegativity of N vs Cl

1-1. (1) Δ*H* = (335 + 467 – 392 – 426) [kJ mol–1] = –16 [kJ mol–1]

(2) Δ*H* = (451 + 467 – 500 – 426) [kJ mol–1] = –8 [kJ mol–1]

1-2. Let BE(Si–Cla) = *x* [kJ mol–1] and BE(Si–Cle) = *y* [kJ mol–1]

From Eq.(2-1): 451 × 4 – (400 + *x* + 3 *y*) = 14; from Eq.(3): 451 × 4 – (2 *x* + 3 *y*) = 50

*x* + 3 *y* = 1390, 2 *x* + 3 *y* = 1754 → *x* = 364, *y* = 342

Answer: BE(Si–Cla) = 364 [kJ mol–1], BE(Si–Cle) = 342 [kJ mol–1]

1-3. (1) A one-step reaction with a larger reaction barrier relative to the silicon case: (2)

(2) A two-step reaction with a small barrier for the first step: (3)

2-1. According to the definition equation: (*χ*A – *χ*B)2 = *D*AB – (*D*AA + *D*BB) / 2

(*χ*N – *χ*H)2 = *D*NH – (*D*NN + *D*HH) / 2

Thus, *D*NH = (*χ*N – *χ*H)2 + (*D*NN + *D*HH) / 2 = (3.04 – 2.10)2 + ((158 / 96.5) + (436 / 96.5)) / 2

= 0.8836 + 3.0777 = 3.961 [eV] = 382 [kJ mol–1]

Similarly, (*χ*Cl–*χ*H)2 = *D*ClH – (*D*ClCl + *D*HH) / 2

Thus, *D*ClCl = 2 × (*D*ClH – (*χ*Cl – *χ*H)2) – *D*HH= 2 × ((426 / 96.5) – (3.16 – 2.1)2) – (436 / 96.5)

= 2 × 3.291 – 4.518 = 2.064 [eV] = 199 [kJ mol–1]

Furthermore, (*χ*Cl–*χ*N)2 = *D*NCl – (*D*ClCl + *D*NN) / 2

Thus, *D*NCl = (*χ*Cl – *χ*N)2 + (*D*ClCl + *D*NN) / 2 = (3.16 – 3.04)2 + (199 / 96.5 + 158 / 96.5) / 2 = 1.864 [eV] = 179.9 [kJ mol–1]

Answer: *D*NH =382 [kJ mol–1]，*D*ClCl =199 [kJ mol–1]，*D*NCl =180 [kJ mol–1].

2-2. Answer: **A**: H2NOH; **B**: HCl; **C**: NH3;**D**: HOCl

Broken bonds: N–Cl (180 [kJ mol–1]), O–H (467 [kJ mol–1])

Formed bonds: N–H (382 [kJ mol–1]), Cl–O (206 [kJ mol–1])

Accordingly, Δ*H* = (180 + 467) – (382 + 206) = 59 [kJ mol–1]

Answer: ***Q*** = 59 [kJ]

2-3. Considering the electron distributions of nitrogen and chlorine below, their *Z*VEeff values can be estimated as follows:

N: (1s)2(2s)2(2p)3, *Z*VEeff(N) = 7 – (0.35×4) – (0.85×2) = 3.9

Cl: (1s)2(2s)2(2p)6(3s)2(3p)5, *Z*VEeff(Cl) = 6.1

Accordingly, their Allred–Rochow electronegativities are:

*χ*AR(N) = 3590×((3.9 – 0.35) / 702) + 0.744 = 3.34

*χ*AR(Cl) = 3590×((6.1 – 0.35) / 992) + 0.744 = 2.85

Thus, the polarity of the N–Cl bond should be considered to be N––Cl+, based on the Allred-Rochow electronegativities.

Problem 15. Sulfur in hot springs and volcanoes

1. Molecular weight of CdS = 144.482

CdS 9.50 [mg] = (9.50 / 144.482) = 6.58×10–5 [mol] → number of moles of H2S

According to the reaction equation: I2 + 2 S2O32– → 2 I– + S4O62–, the number of moles of S2O32– is:

2.50×10–2 × (7.30×10–3) × 2 = 3.65×10–4 [mol]

The mass of sulfur is: (6.58×10–5 + 3.65×10–4 × 2) × 32.068 = 255.2 × 10–4 [g] = 25.5 [mg]

Accordingly, the mass of sulfur in 1 kg of hot spring water is 255 [mg kg–1]

Answer: 255 mg kg–1

2. H2S ⇄ H+ + HS–: *K*1 = 9.50×10–8

HS– ⇄ H+ + S2– : *K*2 = 1.30×10–14

pH = 8.00 corresponds to [H+] = 1.00×10–8 [mol L–1]

Accordingly,

[mol L–1], and

[mol L–1]

Thus, [S2–] + [HS–] + [H2S] = 1.00×10–8 + 7.692×10–3 + 8.097×10–4 = 8.502×10–3 [mol L–1]

The amount of S atoms derived from S2–, HS–, and H2S is:

8.502 × 10–3 × 32.068 = 2.7274 × 10–1 [g] = 272.74 [mg].

The hot spring water contains 5.90 mg of S2O32–, and the mass of the S atoms from S2O32– is:

5.90 × (64.136 / 112.1342) = 3.375 [mg]

Finally, the total amount of sulfur is 272.74 + 3.375 = 276.12 [mg]

Answer: 276 mg kg–1

3. When the volcanic gas is absorbed by the aqueous solution of I2/KI, both the following reactions occur:

H2S + I2 + 2 OH–→ S + 2 H2O +2 I–

SO2 + I2 + 4 OH– → SO42– + 2 I– + 2 H2O

Thus, both H2S and SO2 should react with I2 in a 1:1 ratio.

In the titration test in beaker **B**, the residual I2 should react with sodium thiosulfate as follows:

I2 + 2 S2O32– → 2 I– + S4O62–

The number of moles of sodium thiosulfate consumed is 2.00 ×10–2 × (73.0×10–3) = 1.46 × 10–3 [mol]. Accordingly, the residual amount of I2 in beaker **B** is 1.46 × 10–3 / 2 = 7.30 × 10–4 [mol].

Based on these calculated values, the amount of residual I2 in the initial absorption solution (1.00 L) is 7.30 × 10–3 [mol].

Because the absorption solution contains 2.00 × 10–2 [mol L–1] × 500 [mL] = 1.00 × 10–2 [mol] of I2 before the absorption, 1.00 × 10–2 [mol] – 7.30 × 10–3 [mol] = 2.70 × 10–3 [mol] of I2 was consumed through the gas absorption.

Additionally, 41.5 mg of BaSO4 (molecular weight: 233.3926), i.e., (41.5 × 10–3) / 233 = 1.778 × 10–4 [mol] of BaSO4, was obtained from the reaction in beaker **A**, meaning that 1.778 × 10–4 × 10 = 1.778 × 10–3 mol of SO2 reacted in the absorption solution. Accordingly, when the volcano gas was absorbed into the solution, 1.778 × 10–3 mol of I2 was consumed in the absorption solution. Thus, the amount of I2 consumed by the reaction with H2S is 2.70 × 10–3 – 1.778 × 10–3 = 9.22 × 10–4 mol, which is the same as the amount of H2S absorbed from the volcanic gas.

Considering the combined results, the concentrations of H2S and SO2 in the volcanic gas can be calculated as 9.22 × 10–5 [mol L–1] and 1.78 × 10–4 [mol L–1], respectively.

Answer: [H2S] = 9.22 × 10–5 [mol L–1], [SO2] = 1.78 × 10–4 [mol L–1].

Problem 16. Identification of unknown compounds and allotropes

1-1.

A MgH2

B Mg(OH)2

C MgO

D NH3

1-2. (i) 3Mg + N2 → Mg3N2

(ii) Mg3N2 + 6H2O → 3Mg(OH)2 + 2NH3↑

1-3. 2 mol of NH3 gas is generated from 3 mol of Mg.

2-1.

E 1

F 2

2-2. One cubic unit cell contains 4 molecules of C60, which corresponds to a total of 240 C atoms. Their weight is [g]. The volume of one cubic unit cell is (1.41 × 10−7)3 [cm3]. The density is therefore 1.71 [g cm−3].

2-3.

図形, 矢印

自動的に生成された説明(Tetrahedral structure)

2-4. (iii) O3 + 2KI + H2O → I2 + 2KOH + O2

2-5. *N* [mol] of I2 is generated from *N* [mol] of ozone according to the equation in Q2-4.

In the titration, I2 + 2Na2S2O3 → 2NaI + Na2S4O6.

The required amount of Na2S2O3 = 0.20 × 0.0035 [mol], therefore the amount of I2 is 3.5×10－4 [mol].

2-6. (iv) NO + O3 → NO2 + O2

(v) NO2 + O → NO + O2

(vi) O3 + O → 2O2

Problem 17. Metal Oxides

1-1. {1－(4/3π*r*3×4) / (4*r* / 21/2)3}×100 = 26%

1-2. Octahedral void: (81/2*r*－2*r*) / 2 = 0.05799…　0.0580 nm

Tetrahedral void: (61/2*r*－2*r*) / 2 = 0.03146…　0.0315 nm

1-3. The number of octahedral and tetrahedral voids formed by *n* oxide ions is *n* and 2*n*, respectively. Therefore, the chemical formula is AB2O4 (*x* = 1, *y* = 2, *z* = 4).

1-4.

テーブル, コンピュータ, 写真, 座る が含まれている画像

自動的に生成された説明

2-1. Δ*H*Lexp = (635 + 193 + 498×0.5 + 590 + 1010 + 878 – 141) = 3414 kJ mol–1

2-2.

2-3. Δ*H*Lcalc = 3.47 × 103 kJ mol–1 (answer with three significant digits).

Note that the difference in Δ*H*Lexp and Δ*H*Lcalc is small (less than 1.5%).

Problem 18. Coordination chemistry and its application to solid-state catalysts

1. Theeg orbitals are: and ; the t2g orbitals are: d*xy*, d*yz*, and d*zx*

2. The eg orbitals: +0.6ΔO; the t2g orbitals: –0.4ΔO

3. CFSE d4: –0.6ΔO; d5: 0; d6: –0.4ΔO; d7: –0.8ΔO



**d4 d5 d6 d7**

4.



5.



[kJ mol−1]

6.

**ダイアグラム, 図形, 矢印

自動的に生成された説明** ダイアグラム, 図形

自動的に生成された説明

Mn (group 7) supplies 7 electrons, the five CO ligands supply 10 electrons, and 1 electron is supplied by the neighboring Mn atom, thus satisfying the 18-electron rule. Ir (group 9) supplies 9 electrons, the three CO ligands supply 6 electrons, and 3 electrons are supplied by the neighboring Ir atoms, thus satisfying the 18-electron rule.

7-1. [{(0.55 mL / (R × 273 × 106 /105) mL mol-­1) × 195 g mol-­1} / 0.010 g × 1.0] × 100 = 47.3 % = 47%

7-2. Number of CO molecules (A): (0.55 mL / (R × 273 × 106 /105) mL mol-­1) × (6.02×1023 mol-­1) = 1.463×1019/g-cat

Number of CO molecules per 1.0 g of Pt (B): A / {(0.01×1)} = 1.463×1021/g-Pt

7-3. Surface area per 1 g of Pt (C) [m2 g-­1] = B × (8.0 × 10-­2 nm2) × 10-­18 = 117.0… m2 g-­1 = 117 m2 g-­1

7-4. α: number of Pt metal particles; *r*: radius of a Pt metal particle [m]; *ρ*: density of Pt metal [g cm-­3]

Surface area of 1.0 g of Pt metal (D):{4π*r*2 × α} / 0.01 = C

Volume of 1.0 g of Pt metal (E): {(4/3)π*r*3 × α} / 0.01 = 1 / (*ρ* × 106)

α can be eliminated by taking (E)/(D) to obtain the following equation: *r* / 3 = 1 / (C × *ρ* × 106)

Since *d* [nm] is 2 *r* × 109, *d* = 6000 / (C × *ρ*) = 2.39 nm = 2.4 nm

Problem 19. Acids and bases

1. HClO < HClO2 < HClO3 < HClO4

The more stable the conjugate base, the stronger the acid is. The stability of the conjugate base increase with the number of resonance structures. The number of resonance structures of the conjugate base of oxoacids of chlorine increases in the order of ClO– < ClO2– < ClO3– < ClO4–.

2. 567 + 1312 – 328 = 1551 kJ mol–1

3. 298 + 1312 – 295 = 1315 kJ mol–1

4. |Δ*H*HF| > |Δ*H*HI|, HF < HCl < HBr < HI

5. [Na(H2O)6]+ < [Ca(H2O)6]2+ < [Zn(H2O)6]2+ < [Fe(H2O)6]3+

The strength of aqua acids typically increases with increasing positive charge of the central metal ion and with decreasing ionic radius. The ionic radius decreases moving from left to right in any given period.

6. (i) Lewis acid: BF3; Lewis base: NH3

(ii) Lewis acid: Ni; Lewis base: CO

(iii) Lewis acid: CO2; Lewis base: OH–

(iv) Lewis acid: SiF4; Lewis base: F–

7. The boron atom in H3BO3 is electron deficient; thus, H3BO3 is a Lewis acid and reacts with water via the equation:

H3BO3 + H2O → H+ + B(OH)4–

ダイアグラム

自動的に生成された説明

Problem 20. Semiconductors

1.



2. As the electron configuration of Si is [Ne]3s23p2, the hole-doping of Si requires elements with a smaller number of valence electrons than Si. Therefore, doping Si with B, which has the electron configuration [He]2s22p1,or Ga, which has the configuration [Ar]3d104s24p1, would result in the appearance of p-type properties.

3-1. The following reaction proceeds under an H2 flow, resulting in the loss of oxide ions from TiO2:

TiO2 + *x* H2 → TiO2-*x* + *x* H2O

Accordingly, TiO2 is doped with electrons and the resulting TiO2-*x* exhibits n-type semiconductor properties.

3-2.

1.23 V from Δ*G* = –2*FE*

3-3.

2 H2O + 4 h+ → O2 + 4 H+

3-4. From *E* = *hc*/*λ*

*λ* = 1240/3 = 413 nm

The conversion efficiency is ca. 6.5% when the sunlight spectrum is approximated as shown in the figure below. ⇒ (b)

グラフ

自動的に生成された説明

3-5. *E* = *hc*/*λ* = 1240/350 = 3.543 eV = 5.675×10-19 J

Photon number ＝ (light intensity) / (energy per photon)

＝ 1 [J s-­1] / (5.675×10-19)

＝ 1.762 × 1018

{(0.05×10-6 [mol s-­1] × 2 × 6.02 × 1023)/(1.762 × 1018)} × 100 = 3.42%

Problem 21. Carbenes and non-benzenoid aromatic compounds

図形

中程度の精度で自動的に生成された説明

Similar to the Ruppert-Prakash reagent (Me3SiCF3), Me3Si-CF2Br is converted into a difluorocarbene in the presence of bromide, which attacks the silicon atom. The NMR spectra indicate a symmetric structure for **A**.

図形

低い精度で自動的に生成された説明

Me3SiBr (TMSBr) is generated together with the fluorocarbene. TMSBr then transforms the ketone into a silylenol ether, before a subsequent cyclopropanation affords **B**.

1. The ring-opening of the cyclopropane followed by rearomatization furnishes c.

ダイアグラム, 概略図

自動的に生成された説明

図形

中程度の精度で自動的に生成された説明

**G** is obtained after the addition of a dichlorocarbene to the double bond and the formation of the cyclopropane moiety. Albeit that the stereochemistry is important for the ring-opening, it is not requested here.

図形

中程度の精度で自動的に生成された説明

Based on the molecular formula, only one reduction has occurred.

図形

中程度の精度で自動的に生成された説明 図形

中程度の精度で自動的に生成された説明 図形

中程度の精度で自動的に生成された説明

The whole transformation is shown below, whereby the formation of the intermediary cycloheptatrienyl cation is crucial.

図形

中程度の精度で自動的に生成された説明

図形

中程度の精度で自動的に生成された説明 図形

中程度の精度で自動的に生成された説明

Diaxial ring opening dominates in six-membered ring systems.

Problem 22. Nazarov cyclization

1. a, d

Bicyclic structures that contain rigid five-membered rings rarely engage in a *trans* fusion.

図形

中程度の精度で自動的に生成された説明 図形

中程度の精度で自動的に生成された説明 図形

中程度の精度で自動的に生成された説明

図形

中程度の精度で自動的に生成された説明

Compound **2** is brominated either at the *para*-position or at the *ortho*-position to give **B**. **C** is generated via a halogen-lithium exchange and a subsequent addition to the aldehyde. **D** is obtained from an oxidation of the OH group. **E** is formed via a Nazarov cyclization, followed by deprotonation and aromatization.

Optional problem

ブラシ, 光 が含まれている画像

自動的に生成された説明

Problem 23. Tea party

1. 2*R*, 3*R*

2. HCl, MeOH

3. PhCH2Cl, NaH

4.

**C D E**

図形

中程度の精度で自動的に生成された説明 図形 が含まれている画像

自動的に生成された説明 図形

中程度の精度で自動的に生成された説明

5.

**F G**

図形

中程度の精度で自動的に生成された説明 図形

低い精度で自動的に生成された説明

**H**

図形

中程度の精度で自動的に生成された説明

6. 1) NaH, 2) MeI

7.

**J** (+)-theanine

図形

中程度の精度で自動的に生成された説明 図形

中程度の精度で自動的に生成された説明

Problem 24. *E*-*Z* chemistry

1.

**3** **7**

図形

中程度の精度で自動的に生成された説明 図形

中程度の精度で自動的に生成された説明

2.

図形

中程度の精度で自動的に生成された説明

3.

図形

中程度の精度で自動的に生成された説明

4.

図形

中程度の精度で自動的に生成された説明

5.

**14** **15**

図形

中程度の精度で自動的に生成された説明 図形

中程度の精度で自動的に生成された説明

Problem 25. Fischer indole synthesis

1.

図形

中程度の精度で自動的に生成された説明

2.

図形

中程度の精度で自動的に生成された説明

3.

**14** **15**

**図形

低い精度で自動的に生成された説明 図形

低い精度で自動的に生成された説明**

4.

**17** **18**

図形

低い精度で自動的に生成された説明 図形 が含まれている画像

自動的に生成された説明

5.

図形

低い精度で自動的に生成された説明

6.

図形

低い精度で自動的に生成された説明

Problem 26. Facial chirality

1. **B**, **D**, **E**

Only **C** is a *meso*-compound.

図形

中程度の精度で自動的に生成された説明 図形

低い精度で自動的に生成された説明

**I-1** is a *meso*-compound. (**H-1**, **H-3**), (**H-2**, **H-4**), and (**I-2**, **I-3**) are pairs of enantiomers.

3.

(*R*p)-**J** (*S*p)-**J** (*R*p)-**K** (*S*p)-**K**

図形

低い精度で自動的に生成された説明 図形

低い精度で自動的に生成された説明 図形

低い精度で自動的に生成された説明 図形

低い精度で自動的に生成された説明

**(*R*p)-K** and **(*S*p)-K** are a pair of diastereomers.

4.

図形

中程度の精度で自動的に生成された説明

**M-1** and **M-4** are *meso*-compounds.

Problem 27.Cyclobutadiene

1.

**A B**

**図形

中程度の精度で自動的に生成された説明 図形

中程度の精度で自動的に生成された説明**

**A**; Friedel-Crafts acylation. **B**; Vilsmeier formylation.

Both reactions furnish more electron-deficient products so that the subsequent second substitution is much slower than the first.

2.

図形

中程度の精度で自動的に生成された説明

The reaction is a [2+2]-cycloaddition-like reaction to give a [2.2.0]-bicycle. The stereochemistry is not known exactly, as the reaction mechanism has not yet been elucidated unequivocally. So the stereochemistry is not required. In fact, the cis isomer is produced exclusively on account of the bicyclic ring strain.

3-1.

**図形

中程度の精度で自動的に生成された説明**

The target compound is obtained from a [4+2] cycloaddition reaction followed by decarboxylative aromatization.

3-2.

**G H**

**図形

中程度の精度で自動的に生成された説明 図形

中程度の精度で自動的に生成された説明**

Compound **G** is formed via an electrophilic substitution reaction, wherein Me2N-H works as a leaving group.

図形

中程度の精度で自動的に生成された説明This product (**G’**) was actually obtained (total yield 67%, **G**/**G’** = 3/1)

Compound **H** is an ammonium salt generated *in situ* that undergoes a substitution reaction with an alkoxide.

3-3.

**図形

中程度の精度で自動的に生成された説明**

After demetallation by cerium ammonium nitrate, a [2+2]-cycloaddition-like reaction occurs to give product J. The steric effect of the methyl group and the ring strain can be expected to direct the reaction toward J. Another isomer (J’) might be considered, albeit that its structure would be highly strained given the presence of a double bond at the bridgehead position.

図形

低い精度で自動的に生成された説明

3-4.

**K L**

図形

中程度の精度で自動的に生成された説明 図形

中程度の精度で自動的に生成された説明

The ring-opening metathesis of **J** with ethylene gives **K**, which undergoes the Cope rearrangement to give **L**.

Problem 28. Onion-like complexes

1. 0.120 nm × 6 + 0.143 nm × 12 + 0.140 nm × 12 = 4.116 nm ~ 4.12 nm

4.12 nm / π = 1.31 nm (reported value: 1.32 nm)

2. 0.120 nm × 9 + 0.143 nm × 18 + 0.140 nm × 18 = 6.174 nm ~ 6.17 nm

6.17 nm / π = 1.96 nm (reported value: 1.98 nm)

3. (1.96 nm – 1.31 nm) / 2 = 0.325 nm ~ 0.33 nm

4. The half width of benzene (0.37 nm) is longer than the width of the interspace of the two rings (0.33 nm; *cf.* Q3). Therefore, the benzene ring cannot tilt, which means only configuration C is viable. This conclusion is also applicable to the interspace between benzene and alkyne moieties.

5. 1.31 nm – 0.65 nm = 0.66 nm (reported value: 0.71 nm)

6. Δ*G* = –*RT*ln*K*

*K =* 814 × 102

*K* = (1–*a*)/*ca*2

where *a* is the ratio of free [6]CPP (= free [11]CPP) and *c* the total concentration of [6]CPP.

In this case, *c* = 0.400 mmol L-1 as two solutions are mixed in the same volume ratio.

This affords *a* = 0.690 and consequently

[free [6]CPP] = *ca* = 2.76×10–4 mol L–1

7. (a) and (d) are correct.

b: The [*n*]CPPs (*n* = 9-12) do not quantitatively form complexes because their peaks remain unchanged after the addition of the second equivalent of [13]CPP.

c: As the complex precipitates from the solution, its peak must vanish.

e: The peak attributed to [8]CPP disappears after the addition of the first equivalent of [13]CPP. The new peak should thus be ascribed exclusively to [13]CPP.

Problem 29. Hydrogen-bonded capsules

1.



2. (b)

3. (c)

The graph shows that two equivalents of DBU (0.5 mmol) lead to the complete dimerization of **D**. Accordingly, every molecule contains two deprotonated sites and each dimeric capsule of **D** should contain four deprotonated sites.

In the original report, this graph was obtained in the presence of pyrazine; this divergence can be ignored here.

4.

*a* = 0.85

Thus, 85% of pyrazine is encapsulated by D.

5. (a): (1)

The OH groups are acetylated, which leads to the retro-dimerization of the capsule and hence the release of benzene.

(b): (3)

Upon dilution with chloroform, chloroform is gradually encapsulated under concomitant release of benzene.

6. The reaction **B**→**C** affords a methylene-bridged capsule. Due to this covalent bridging, reversible association and dissociation is not possible anymore, and the guest molecule can no longer be released.

Problem 30. Synthesis and structural analysis of polymers

1.



2. (b)

3. (1) g A  
(2) d B  
(3) a D

4. C

5. *d*[M1]/*d*[M2] = [M1]/[M2]×(*r*1[M1]+[M2])/([M1]+*r*2[M2])  
As the content of M1 in the polymer is 50 mol%, *d*[M1]/*d*[M2] = 1.0, *r*1 = 0.40, and *r*2 = 0.10 can be substituted into the above equation:  
1.0 = [M1]/[M2]× (0.40[M1]+[M2])/([M1]+0.10[M2])  
[M2]×([M1]+0.10[M2]) = [M1]×(0.40[M1]+[M2])   
0.10[M2]2 = 0.40[M1]2  
([M1]/[M2])2 = 0.10/0.40 = 0.25  
[M1]/[M2]= 0.50

Therefore, the content of M1 in the total monomer mixture ([M1]/([M1]+[M2])) is 1/3.  
33 mol%

6. Polymer obtained:

**1** B

**2** D

Site where the initiator reacts:

**1** F

**2** G

Problem 31. Total synthesis of tetrodotoxin

1.

**2** **6**

** **

2.

**9** **10**

3.

**12** **13** **15**

**ダイアグラム

自動的に生成された説明 ダイアグラム, 概略図

自動的に生成された説明 図形

中程度の精度で自動的に生成された説明**

**17** **18**

**図形

中程度の精度で自動的に生成された説明 図形

中程度の精度で自動的に生成された説明**

**19**

**図形

中程度の精度で自動的に生成された説明**

4.

**21 23**

図形

中程度の精度で自動的に生成された説明 図形

中程度の精度で自動的に生成された説明

Task 1. Analysis of the saponification rate using a pH meter

1.

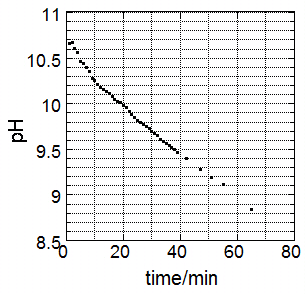
|  |  |
| --- | --- |
| *C*1 [mol L-1] | *C*2 [mol L-1] |
| When 88.1 mg of ethyl acetate is used | When the concentration of aqueous solution of NaOH is 0.05005 mol L–1: |

2. CH3COOC2H5 + NaOH → CH3COONa + C2H5OH

3.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Time (minutes) | Temperature (℃) | pH | Time (minutes) | Temperature (℃) | pH |
| 5 |  | 10.46 | 35 |  | 9.56 |
| 10 |  | 10.26 | 40 |  | 9.45 |
| 15 |  | 10.11 | 47 |  | 9.28 |
| 20 |  | 9.81 | 51 |  | 9.19 |
| 25 |  | 9.82 | 55 |  | 9.11 |
| 30 |  | 9.70 | 65 |  | 8.84 |

4.



The slope is

Therefore,

5. The concentration of ethyl acetate after mixing is

6.

Task 2. Simultaneous acid–base titration

1. NaOH + HCl → NaCl + H2O

Na2CO3 + HCl → NaCl + NaHCO3

2. NaHCO3 + HCl → NaCl + H2O + CO2

3. NaOH [g]： [g]

Na2CO3 [g]： [g]

4. The horizontal axis is the amount of the standard solution added, while the vertical axis is the pH value of the unknown alkali solution. The following figure shows the actual measurement data (unknown alkali solution: 30.00 mL) where the unknown alkali solution was prepared from 1.0 L distilled water containing 0.5 g of NaOH and 2.5 g of Na2CO3.

グラフ が含まれている画像

自動的に生成された説明

Task 3. Synthesis and analysis of a cobalt(III) oxalate complex

1-4 The concentration of the potassium permanganate aqueous solution *c* is given by

*c* = w×2/134/5/v×1000

where w is the weight of sodium oxalate used in step B-1 and v is the volume of the aqueous potassium permanganate solution (accepted) used in the titration in step B-1.

2. 5 Na2C2O4 + 2 KMnO4 + 8 H2SO4 → K2SO4 + 2 MnSO4 + 5 Na2SO4 + 10 CO2 + 8 H2O

3. The weight% of the oxalate ion is given by

*c* × x/1000 × 5/2 × 88/y × 100

where *c* is the concentration of the potassium permanganate aqueous solution determined above, x is the volume of the potassium permanganate aqueous solution (accepted) used in the titration in step B-2 and y is the weight of cobalt oxalate complex analyzed in step B-2.

From the table below, if the weight% of oxalate ion is more than 50.8% (=(53.4+48.3)/2), the product can be estimated to be a tris complex. Thus, cobalt ion to oxalate ligand composition ratio is 1:3.

Compound composition Molecular weight Weight% of oxalate ion

tris complex: K3[Co(C2O4)3]•3H2O 494.3 53.4 %

bis complex: K[Co(C2O4)2(H2O)2]•3H2O 364.1 48.3 %

mono complex: [Co(C2O4)Cl(H2O)3]•3H2O 290.5 30.3 %

4. The molecular weight of cobalt(II) chloride hexahydrate is 238 g/mol. If it is estimated that a tris complex was formed, the yield is given by

z/494.3×238×100

where z is the weight of the crystals of the complex obtained in step A.

Task 4. Hinokitine: synthesis of a deep-red-colored natural product

1. Hinokitine is a 3:1 complex of hinokitiol and iron(III) ion with the molecular formula (MF) C30H33FeO6 and a molecular weight (MW) of 545.43 g mol-1. The theoretical yield of hinokitine can be calculated from the amounts of the reactants hinokitiol (MF = C10H12O2 and MW = 164.20) and iron(III) nitrate nonahydrate (MF = FeH18N3O18 and MW = 403.99) used in the synthesis.



2. Nitric acid (HNO3)

3. There are 8 isomers in total, including enantiomers (*D* and *L*) of hinokitine, depending on the position of the isopropyl groups (right or left)



(right, right, right) (left, left, left)



(right, right, left) (left, left, right)



(right, left, left) (left, right, right)



(left, left, left) (right, right, right)

Task 5. Functionalization of a seven-membered ring: synthesis of tropolone tosylate

1.



4-Dimethylaminopyridine (DMAP) acts as a Brønsted base in this reaction. A tropolonate salt, 4-dimethylaminopyridinium tropolonate, is formed by proton transfer from the hydroxy group of tropolone to the nitrogen atom of the pyridine ring of DMAP. Tropolonate has an aromatic nature originating from the contribution of the canonical form with a tropylium ion structure (**C**).



DMAP is more basic than pyridine due to the electron-donating effect of the dimethylamino group at the 4-position. The dimethylamino group can stabilize the positive charge on the protonated DMAP with the possible resonance structure (**E**).



2. After the tosylation, DMAP is transformed into DMAP hydrochloride, [(DMAP)H][Cl], which is soluble in water. The typical procedure for the recovery of DMAP is as follows. An appropriate organic solvent and water are added to the reaction mixture. While the organic layer mainly contains tropolone tosylate, the aqueous layer contains the DMAP hydrochloride. The aqueous layer is basified with an aqueous solution of sodium hydroxide (NaOH) followed by extraction into an appropriate organic solvent. The organic layer is dried over anhydrous sodium sulfate (Na2SO4) and evaporated under vacuum to afford solid DMAP. Sufficiently pure DMAP can be obtained using a further purification technique, such as crystallization from an appropriate organic solvent or chromatography on silica gel using an appropriate organic solvent as the eluent.

3.



There are two tosylation products of hinokitiol (**F** and **G**), which are isomers. Hinokitiol is deprotonated by DMAP in a fashion similar to tropolone, affording the isopropyl-substituted tropolonate with three possible resonance forms (**H**, **I**, and **J**, which are analogous to **A**, **B**, and **C**). The products **F** and **G** are formally obtained from the reaction of **H** and **I** with tosyl chloride (TsCl), respectively.



Task 6. Hydrolysis of polyethylene terephthalate: A small experiment for us, but a giant leap toward a more sustainable society

1.



2. The theoretical weight of A can be calculated using the following equation:



The yield of A based on the amount of PET used can be calculated using the following equation:



3. The yield of A based on the amount of PET reacted can be calculated using the following equation:



4.



5. As shown above, the first and the second steps are reversible. On the other hand, the final step is not reversible, because the neutralization reaction between the acidic carboxyl group and the highly basic alkoxide gives a carboxylate, which is not sufficiently basic to regenerate the alkoxide by deprotonation of the hydroxyl group. The irreversible nature of the final step makes the overall system irreversible. In addition, the hydroxyl group, which is much less nucleophilic than the alkoxide, is not able to attack the carbonyl group to induce the backward condensation reaction. Another reason is the poor solubility of the resulting disodium terephthalate, which precipitates from solution, which shifts the equilibrium toward the formation of the products.

6. Under the same conditions, the hydrolysis conducted in this experiment is much more efficient than the hydrolysis of the polyamide. The carbonyl carbon atom of the amide group is less electrophilic than that of the ester group on account of the greater extent of delocalization of the lone pair on the nitrogen atom compared to the lone pair on the oxygen. Consequently, the carbonyl carbon atom of the amide group is more resistant to the nucleophilic addition of the hydroxide ion than the ester group. Moreover, even if the nucleophilic addition of the hydroxide ion (-OH) took place, the resulting intermediate would preferentially release -OH rather than the amide anion (-NHR), which is much more basic than -OH and thus more difficult to produce. In other words, the intermediate preferentially dissociates to recover the amide bond.

Task 7. Separation of blue and red components from a green mixture

1. 4-(phenylazo)phenol

Recrystallization is effective or available when (1) the desired compound is major in the mixture and when (2) the desired compound is more easily crystallized than the impurity. The recrystallization of the 'mixture' for the column chromatography (1:1 mixture) to separate 4-(phenylazo)phenol will be unsuccessful.

2. Guaiazulene from the first colored fraction (blue) and 4-(phenylazo)phenol from the second colored fraction (orange).

3. Recrystallization is conducted by the difference of solubility at different temperatures. Although the solubility of the substance would decrease at lower temperature, it does not drop to zero. Because of some solubility of the substance at lower temperature, the yield of recrystallization cannot be quantitative.

4. Guaiazulene eluted first, and 4-(phenylazo)phenol eluted later. This means that 4-(phenylazo)phenol exhibits higher interaction (affinity) with the stationary phase, silica gel. The hydroxy group interacts with the OH group on the surface of the silica gel via hydrogen bonding. Nitrogen atoms in 4-(phenylazo)phenol may also contribute the interaction, although the basicity of sp2 nitrogen is low, and strong interaction is not expected from the azo group. It should be noted the azobenzene itself is a neutral compound, and exhibits low affinity with silica gel.

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