SGP-4 C-0 C Alphonsus Neo

SGP-4 C-0 C-1

IChO General instructions Cover sheet

Please return this cover sheet together with all the related question sheets.



SGP-4 C-0 G-1



International Chemistry Olympiad 2021 Japan 53rd IChO2021 Japan 25th July – 2nd August, 2021 https://www.icho2021.org







General Instruction

- You are allowed to use only pen to write the answer.
- Your calculator must be non-programmable.
- This examination has **9 problems**.
- You can solve the problems in any order.
- You will have **5 hours** to solve all problems.
- You can **begin** working only after the **START** command is given.
- All results must be written in the appropriate answer boxes with pen on the **answer sheets**. Use the back of the question paper if you need scratch paper. **Answers written outside the answer boxes will not be graded.**
- Write relevant calculations in the appropriate boxes when necessary. Full marks will be given for correct answers only when your work is shown.
- The invigilator will announce a **30-minute** warning before the **STOP** command.
- You **must stop** working when the **STOP** command is given. Failure to stop writing will lead to the nullification of your examination.
- The official English version of this examination is available on request only for clarification.
- You are not allowed to leave your working place without permission. If you need any assistance (broken calculator, need to visit a restroom, etc), raise your hand and wait until an invigilator arrives.

GOOD LUCK!

Problems and Grading Information

	Title	Total Score	Percentage
1	Hydrogen at a Metal Surface	24	11
2	Isotope Time Capsule	35	11
3	Lambert–Beer Law?	22	8
4	The Redox Chemistry of Zinc	32	11
5	Mysterious Silicon	60	12
6	The Solid-State Chemistry of Transition Metals	45	13
7	Playing with Non-benzenoid Aromaticity	36	13
8	Dynamic Organic Molecules and Their Chirality	26	11
9	Likes and Dislikes of Capsules	23	10
		Total	100



Physical Constants and Equations

Constants

Speed of light in vacuum	$c = 2.99792458 \times 10^8 \mathrm{m \ s^{-1}}$
Planck constant	$h = 6.62607015 \times 10^{-34} \mathrm{J \ s}$
Elementary charge	$e = 1.602176634 \times 10^{-19} \mathrm{C}$
Electron mass	$m_{\rm e} = 9.10938370 \times 10^{-31}{\rm kg}$
Electric constant (permittivity of vacuum)	$\varepsilon_0 = 8.85418781 \times 10^{-12} \mathrm{F} \mathrm{m}^{-1}$
Avogadro constant	$N_{\rm A} = 6.02214076 imes 10^{23} { m mol}^{-1}$
Boltzmann constant	$k_{\rm B} = 1.380649 \times 10^{-23} {\rm J} {\rm K}^{-1}$
Faraday constant	$F = N_{\rm A} \times e = 9.64853321233100184 \times 10^4 {\rm C \ mol^{-1}}$
Gas constant	$R = N_{\rm A} \times k_{\rm B} = 8.31446261815324 \; {\rm J} \; {\rm K}^{-1} \; {\rm mol}^{-1}$
Gas constant	$= 8.2057366081 imes 10^{-2} { m L} { m atm} { m K}^{-1} { m mol}^{-1}$
Unified atomic mass unit	$u = 1 \text{ Da} = 1.66053907 \times 10^{-27} \text{ kg}$
Standard pressure	$p = 1 \operatorname{bar} = 10^5 \operatorname{Pa}$
Atmospheric pressure	$p_{atm} = 1.01325 imes 10^5 Pa$
Zero degree Celsius	$0 ^{\circ}\mathrm{C} = 273.15 \mathrm{K}$
Ångstrom	$1 \text{ Å} = 10^{-10} \text{ m}$
Picometer	$1 \mathrm{pm} = 10^{-12} \mathrm{m}$
Electronvolt	$1 \mathrm{eV} = 1.602176634 \times 10^{-19} \mathrm{J}$
Part-per-million	$1 \mathrm{ppm} = 10^{-6}$
Part-per-billion	$1 ppb = 10^{-9}$
Part-per-trillion	$1 \mathrm{ppt} = 10^{-12}$
pi	$\pi = 3.141592653589793$
The base of the natural logarithm (Euler's number)	e = 2.718281828459045





Equations

The ideal gas law	PV = nRT
-	, where P is the pressure, V is the volume, n is the amount of substance,
	T is the absolute temperature of an ideal gas.
Coulomb's law	$F = k_{e} \frac{q_1 q_2}{r^2}$
	, where F is the electrostatic force, $k_{\rm e}(\simeq 9.0\times 10^9{\rm Nm^2C^{-2}})$ is Coulomb's constant, q_1 and q_2 are the magnitudes of the charges, and r is the distance between the charges.
The first law of thermo-	$\Delta U = q + w$
dynamics	, where ΔU is the change in the internal energy, q is the heat supplied, w is the work done.
Enthalpy H	H = U + PV
Entropy based on Boltz-	$S = k_{B} \ln W$
mann's principle <i>S</i>	, where W is the number of microstates.
The change of entropy	$\Delta S = \frac{q_{rev}}{T}$
ΔS	, where $q_{\sf rev}$ is the heat for the reversible process.
Gibbs free energy G	G = H - TS
	$\Delta_{r}G^{\circ} = -RT\ln K = -zFE^{\circ}$
	, where K is the equilibrium constant, z is the number of electrons, E° is
	the standard electrode potential.
Reaction quotient Q	$\Delta_{\rm r}G = \Delta_{\rm r}G^\circ + RT\ln Q$
	For a reaction
	$aA + bB \rightleftharpoons cC + dD$
	$Q = \frac{[C]^{\circ}[D]^{\circ}}{1}$
	$\begin{bmatrix} A \end{bmatrix}^a \begin{bmatrix} B \end{bmatrix}^b$
	, where [A] is the concentration of A.





Heat change Δq	$\Delta q = nc_{m}\Delta T$, where c_{m} is the temperature-independent molar heat capacity.
Nernst equation for re- dox reaction	$E = E^{\circ} + \frac{RT}{zF} \ln \frac{C_{ox}}{C_{red}}$, where C_{ox} is the concentration of oxidized substance, C_{red} is the concentration of reduced substance.
Arrhenius equation	$\begin{aligned} k &= A \exp\left(-\frac{E_a}{RT}\right)\\ \text{, where }k \text{ is the rate constant, }A \text{ is the pre-exponential factor, }E_a \text{ is the activation energy.}\\ \exp(x) &= e^x \end{aligned}$
Lambert–Beer equation	$A = \varepsilon lc$, where A is the absorbance, ε is the molar absorption coefficient, l is the optical path length, c is the concentration of the solution.
Henderson–Hasselbalch equation	For an equilibrium $HA \rightleftharpoons H^+ + A^-$, where equilibrium constant is K_a , $pH = pK_a + \log\left(\frac{[A^-]}{[HA]}\right)$
Energy of a photon	$E = h\nu = h\frac{c}{\lambda}$, where ν is the frequency, λ is the wavelength of the light.
The sum of a geometric series	When $x \neq 1$, $1 + x + x^2 + \dots + x^n = \sum_{i=0}^n x^i = \frac{1 - x^{n+1}}{1 - x}$
Approximation equation that can be used to solve problems	When $x \ll 1$, $\frac{1}{1-x} \simeq 1+x$



G 6 SGP English (Singapore)

SGP-4 C-0 G-6

Periodic Table

	_	<u> </u>															_													
4	0	Fe ∝	Helium 4.003	10	Ne	Neon	20.180	18	Ar	Argon 39.948	36	Ϋ́	Krypton 83.798	54	Xe	Xenon	131.293	86	Я	Radon [222]	118	og	Oganesson [294]							
17	-			6	ш	Fluorine	18.998	17	ō	Chlorine 35.452	35	Ъ	Bromine 79.904	23	_	lodine	126.904	85	At	Astatine [210]	117	Ts	Tennessine [293]	71	Г	Lutetium	174.967	103	2	Lawrencium [262]
16	0			8	0	Oxygen	15.999	16	S	sulfur 32.068	34	Se	Selenium 78.971	52	Te	Tellurium	127.60	84	Ро	Polonium [210]	116	Ľ	Livermorium [293]	20	٩Y	Ytterbium	173.045	102	No	Nobelium [259]
ц Т	<u>.</u>			2	z	Nitrogen	14.007	15	۵.	Phosphorus 30.974	33	As	Arsenic 74.922	51	Sb	Antimony	121.760	83	Ξ	Bismuth 208.98	115	Mc	Moscovium [289]	69	Tm	Thulium	168.934	101	Md	Mendelevium [258]
4	<u>+</u>			9	ပ	Carbon	12.011	14	S:	silicon 28.085	32	Ge	Germanium 72.630	50	Sn	Tin	118.710	82	Po	Lead 207.2	114	Ē	Flerovium [289]	68	ш	Erbium	167.259	100	Еm	Fermium [257]
13	2			s	В	Boron	10.814	13	F	Aluminium 26.982	31	Ga	Gallium 69.723	49	Ч	Indium	114.818	81	F	Thallium 204.384	113	ЧN	Nihonium [278]	67	Р	Holmium	164.930	66	Es	Einsteinium [252]
40	2			_							30	Zn	Zinc 65.38	48	g	Cadmium	112.414	80	Ъ	Mercury 200.592	112	ö	Copernicium [285]	99	Ŋ	Dysprosium	162.500	98	ŭ	Californium [252]
++	=						active element]				59	Cu	Copper 63.546	47	Ag	Silver	107.868	62	Au	Gold 196.967	111	Вg	Roentgenium [280]	65	Tb	Terbium	158.925	67	剐	Berkelium [247]
UF	2						s for the radios				28	Ī	Nickel 58.693	46	Ъd	Palladium	106.42	78	£	Platinum 195.084	110	Ds	Darmstadtium [281]	64	Gd	Gadolinium	157.25	96	Cm	curium [247]
σ	n						[in parenthesi				27	ပိ	Cobalt 58.933	45	ЧЧ	Rhodium	102.906	22	<u>۲</u>	Indium 192.217	109	Mt	Meitnerium [276]	63	Еu	Europium	151.964	95	Am	Americium [243]
α	0			atomic number	Symbol	name	atomic weight				26	Fe	Iron 55.845	44	Ru	Ruthenium	101.07	76	So	^{Osmium} 190.23	108	Hs	Hassium [277]	62	Sm	Samarium	150.36	94	Pu	Plutonium [239]
2			Key:	113	Ч	Nihonium	[278]				25	Мп	Manganese 54.938	43	Tc	Technetium	[66]	75	Re	Rhenium 186.207	107	Bh	Bohrium [272]	61	Рп	Promethium	[145]	93	ЧN	Neptunium [237]
ų	D										24	ວັ	Chromium 51,996	42	Мо	Molybdenum	95.95	74	≥	Tungsten 183.84	106	Sg	Seaborgium [271]	60	ΡŊ	Neodymium	144.242	92	⊃	Uranium 238.029
Ľ	n										23	>	Vanadium 50.942	41	qN	Niobium	92.906	73	Та	Tantalum 180.948	105	Db	Dubnium [268]	59	ጘ	Praseodymium	140.908	91	Ра	Protactinium 231.036
	t										22	Ħ	Titanium 47.867	40	Zr	Zirconium	91.224	72	Έ	Hafhium 178.49	104	Ŧ	Rutherfordium [267]	58	oe	Cerium	140.116	06	Th	Thorium 232.038
¢	0										21	Sc	Scandium 44.956	39	≻	Yttrium	88.906	57-71	La-Lu	Lanthanoids	89-103	Ac-Lr	Actinoids	57	La	Lanthanum	138.905	68	Ac	Actinium [227]
•	V			4	Be	Beryllium	9.012	12	Mg	Magnesium 24.306	20	Ca	Calcium 40.078	38	ي ک	Strontium	87.62	56	Ba	Barium 137.327	88	Ra	Radium [226]	57-71	La-Lu	Lanthanoids		89-103	Ac-Lr	Actinoids
-	-	- I	Hydrogen 1.008	e	:	Lithium	6.968	÷	Na	Sodium 22.990	19	¥	Potassium 39.098	37	Rb	Rubidium	85.468	55	S	caesium 132.905	87	ц	Francium [223]							



SGP-4 C-0 G-7

¹H NMR Chemical Shifts



 $\Delta \delta$ for one alkyl group-substitution: *ca.* +0.4 ppm

SGP-4 C-1 C Alphonsus Neo

SGP-4 C-1 C-1



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Hydrogen at a Metal Surface

11 % of the total								
Question	A.1	A.2	B.1	B.2	B.3	B.4	Total	
Points	6	4	5	3	3	3	24	
Score								

SGP-4 C-1 Q-1



Hydrogen is expected to be a future energy source that does not depend on fossil fuels. In this problem, we will consider the hydrogen-storage process in a metal, which is related to hydrogen transport and storage technology.

Part A

As hydrogen is absorbed into the bulk of a metal via its surface, let us first consider the adsorption process of hydrogen at the metal surface, $H_2(g) \rightarrow 2H(ad)$, where the gaseous and adsorbed states of hydrogen are represented as (g) and (ad), respectively.

Hydrogen molecules (H₂) that reach the metal surface (M) dissociate at the surface and are adsorbed as H atoms (Fig. 1). The potential energy of H₂ is represented by two variables: the interatomic distance, d, and the height relative to the surface metal atom, z. It is assumed that the axis along the two H atoms is parallel to the surface and that the center of gravity is always on the vertical dotted line in Fig. 1.

Fig. 2 shows the potential energy contour plot for the dissociation at the surface. The numerical values represent the potential energy in units of kJ per mole of H_2 . The solid line spacing is 20 kJ mol⁻¹, the dashed line spacing is 100 kJ mol⁻¹, and the spacing between solid and dashed lines is 80 kJ mol⁻¹. The zero-point vibrational energy is ignored.



Q1-2 SGP English (Singapore)



SGP-4 C-1 Q-2









6pt

A.1 For part (i) to (iii), <u>select</u> the closest value from A–G.
(i) The interatomic distance for a gaseous H₂ molecule
(ii) The interatomic distance between metal atoms (d_M in Fig. 1)
(iii) The distance of adsorbed H atoms from the surface (h_{ad} in Fig. 1)

A. 0.03 nmB. 0.07 nmC. 0.11 nmD. 0.15 nmE. 0.19 nmF. 0.23 nmG. 0.27 nm

A.2For part (i) and (ii), select the closest value from A-H.
(i) the energy required for the dissociation of gaseous H2 to gaseous H
 $[H_2(g) \rightarrow 2H(g)]$
(ii) the energy released during the adsorption of a gaseous H2 $[H_2(g) \rightarrow 2H(ad)]$ 4ptA. 20 kJ mol⁻¹B. 40 kJ mol⁻¹C. 60 kJ mol⁻¹D. 100 kJ mol⁻¹E. 150 kJ mol⁻¹F. 200 kJ mol⁻¹G. 300 kJ mol⁻¹H. 400 kJ mol⁻¹



SGP-4 C-1 Q-4



Part B

The adsorbed hydrogen atoms are then either absorbed into the bulk, or recombine and desorb back into the gas phase, as shown in the reactions (1a) and (1b). H(ab) represents a hydrogen atom absorbed in the bulk.

$$H_2(g) \stackrel{k_1}{\underset{k_2}{\longleftrightarrow}} 2H(ad)$$
(1a)

$$H(ad) \xrightarrow{k_3} H(ab)$$
(1b)

The reaction rates per surface site for adsorption, desorption, and absorption are $r_1[s^{-1}], r_2[s^{-1}]$ and $r_3[s^{-1}]$, respectively. They are expressed as:

$$r_1 = k_1 P_{\mathsf{H}_2} (1 - \theta)^2 \tag{2}$$

$$r_2 = k_2 \theta^2 \tag{3}$$

$$r_3 = k_3 \theta \tag{4}$$

where $k_1 [s^{-1} Pa^{-1}], k_2 [s^{-1}]$ and $k_3 [s^{-1}]$ are the reaction rate constants and P_{H_2} is the pressure of H₂.

Among the sites available on the surface, θ ($0 \le \theta \le 1$) is the fraction occupied by H atoms. It is assumed that the rates of adsorption and desorption are significantly faster than rate of absorption ($r_1, r_2 \gg r_3$) and θ remains constant.

B.1 r_3 can be expressed as: 5pt $r_3 = \frac{k_3}{1 + \sqrt{\frac{1}{P_{H_2}C}}}$ (5) <u>Express</u> C in terms of k_1 and k_2 .



A metal sample with a surface area of $S = 1.0 \times 10^{-3} \text{ m}^2$ was placed in a container (1L = $1.0 \times 10^{-3} \text{ m}^3$) with H₂ ($P_{\text{H}_2} = 1.0 \times 10^2 \text{ Pa}$). The density of hydrogen-atom adsorption sites on the surface was $N = 1.3 \times 10^{18} \text{ m}^{-2}$. The surface temperature was kept at T = 400 K.

As reaction (1) proceeded, P_{H_2} decreased at a constant rate of $v = 4.0 \times 10^{-4} \text{ Pa s}^{-1}$. It is assumed that H₂ is an ideal gas and the volume of the metal sample is negligible.

- **B.2** Calculate the amount of H atoms in moles absorbed per unit area of the surface 3pt per unit time, $A \text{ [mol s}^{-1} \text{ m}^{-2} \text{]}$.
- **B.3** At T = 400 K, $C = 1.0 \times 10^2$ Pa⁻¹. <u>Calculate</u> the value of k_3 at 400 K. If you did 3pt not obtain the answer to **B.2**, use $A = 3.6 \times 10^{-7}$ mol s⁻¹ m⁻².
- **B.4** At a different T, $C = 2.5 \times 10^3 \text{ Pa}^{-1}$ and $k_3 = 4.8 \times 10^{-2} \text{ s}^{-1}$ are given. For the plot 3pt of r_3 as a function of P_{H_2} at this temperature, **select** the correct plot from option (a)–(h).





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SGP-4 C-1 A-1

Hydrogen at a Metal Surface

Part A

A.1 (6 pt)

(i) (ii) (iii)

A.2 (4 pt)







Part B

B.1 (5 pt) *C* = **B.2** (3 pt)

SGP-4 C-1 A-2

 $\underline{A} = \mod \mathrm{s}^{-1} \mathrm{m}^{-2}$





B.3 (3 pt)	
$k_3 =$	
B.4 (3 pt)	

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SGP-4 C-2 C-1



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Isotope Time Capsule

11 % of the total							
Question	A.1	A.2	A.3	A.4	Total		
Points	8	8	10	9	35		
Score							



Molecular entities that differ only in isotopic composition, such as CH_4 and CH_3D , are called isotopologues. Isotopologues are considered to have the same chemical characteristics. However, in nature there exists a slight difference between them.

It is assumed that all of the substances shown in this Question are in gaseous phase.

Let us consider the following equilibrium:

The entropy, *S*, increases with increasing number of possible microscopic states of a system, *W*:

$$S = k_{\rm B} \ln W \tag{2}$$

W = 1 for ${}^{12}C^{16}O_2$ and ${}^{12}C^{18}O_2$.

In contrast, W = 2 for a ${}^{12}C^{16}O^{18}O$ molecule because the oxygen atoms are distinguishable in this molecule. As the right-hand side of the equilibrium shown in eq. 1 has two ${}^{12}C^{16}O^{18}O$ molecules, $W = 2^2 = 4$.



A.1The enthalpy change,
$$\Delta H$$
, of eq. 3 is positive regardless of the temperature.8pt $H_2 + DI \rightleftharpoons HD + HI$ (3)Calculatethe equilibrium constants, K , for eq. 3 at very low (as $T \rightarrow 0$) and very high (as $T \rightarrow +\infty$) temperatures.
You may assume that the reaction remains unchanged at these temperatures and that ΔH converges to a constant value for high temperatures.

The ΔH of the following process can be explained by molecular vibrations.

$$2\mathsf{H}\mathsf{D} \rightleftharpoons \mathsf{H}_2 + \mathsf{D}_2 \qquad \qquad K = \frac{[\mathsf{H}_2][\mathsf{D}_2]}{[\mathsf{H}\mathsf{D}]^2} \tag{4}$$

At T = 0 K, the vibrational energy of a diatomic molecule whose vibration frequency is $\nu [s^{-1}]$ is expressed as:

$$E = \frac{1}{2}h\nu$$
(5)

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \tag{6}$$

where k is the force constant and μ is the reduced mass, which is expressed in terms of the mass of the two atoms in the diatomic molecule, m_1 and m_2 , according to:

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \tag{7}$$

A.2 The vibration of H_2 is at 4161.0 cm⁻¹ when reported as a wavenumber. 8pt <u>**Calculate**</u> the ΔH of the following equation at T = 0 K in units of J mol⁻¹.

$$2HD \rightarrow H_2 + D_2 \tag{8}$$

It is assumed that:

- only the vibrational energy contributes to the ΔH .
- the k values for H₂, HD, and D₂ are identical.
- the mass of H is 1 Da and the mass of D is 2 Da.





The molar ratio of H_2 , HD, and D_2 depends on the temperature in a system in equilibrium. Here, Δ_{D_2} is defined as the change of the molar ratio of D_2 .

$$\Delta_{\mathsf{D}_2} = \frac{R_{\mathsf{D}_2}}{R_{\mathsf{D}_2}^*} - 1 \tag{9}$$

where R_{D_2} refers to $\frac{[D_2]}{[H_2]}$ in the sample and $R_{D_2}^*$ to $\frac{[D_2]}{[H_2]}$ at $T \to +\infty$. It should be noted that the distribution of isotopes becomes random at $T \to +\infty$.

A.3 <u>**Calculate**</u> Δ_{D_2} when the isotopic exchange is in equilibrium at the temperature 10pt where *K* in eq. 4 is 0.300. It is assumed that the natural abundance ratios of D and H are 1.5576×10^{-4} and $1 - 1.5576 \times 10^{-4}$, respectively.





A doubly substituted isotopologue contains two heavy isotope atoms in one molecule.

In general, the molar ratio of the doubly substituted isotopologue increases with decreasing temperature.

Let us consider the molar ratio of CO_2 molecules with molecular weights of 44 and 47, which are described as $CO_2[44]$ and $CO_2[47]$. The quantity Δ_{47} is defined as:

$$\Delta_{47} = \frac{R_{47}}{R_{47}^*} - 1 \tag{10}$$

 R_{47} refers to $\frac{[CO_2[47]]}{[CO_2[44]]}$ in the sample and R_{47}^* to $\frac{[CO_2[47]]}{[CO_2[44]]}$ at $T \to +\infty$. The natural abundances of carbon and oxygen atoms are shown below; ignore any other isotopes that are not shown.

	¹² C	¹³ C
natural abundance	0.988888	0.011112

	¹⁶ O	¹⁷ O	¹⁸ O
natural abundance	0.997621	0.0003790	0.0020000

The temperature dependence of Δ_{47} is determined as follows, where T is given as the absolute temperature in units of K:

$$\Delta_{47} = \frac{36.2}{T^2} + 2.920 \times 10^{-4} \tag{11}$$

A.4 The R_{47} of fossil plankton obtained from the Antarctic seabed was 4.50865×10^{-5} . 9pt **Estimate** the temperature using this R_{47} . This temperature is interpreted as the air temperature during the era in which the plankton lived. You only need to consider the most common isotopologue of $CO_2[47]$ for the calculation.





Isotope Time Capsule

A.1 (8 pt) $T \rightarrow 0: K = , T \rightarrow +\infty: K =$





A.2 (8 pt)	
$\Delta H =$	J mol ⁻¹





A.3 (10 pt) $\Delta_{\rm D_2} =$





A.4 (9 pt)	
<u>T</u> =	<u>_K</u>

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SGP-4 C-3 Q-1

Lambert-Beer Law?

8 % of the total						
Question	A.1	B.1	B.2	Total		
Points	10	6	6	22		
Score						

In this problem, you can ignore the absorption of the cell and the solvent. The temperatures of all solutions and gases are kept constant at 25 °C.

Part A

An aqueous solution **X** was prepared using HA and NaA. The concentrations [A⁻], [HA], and [H⁺] in solution **X** are 1.00×10^{-2} mol L⁻¹, 1.00×10^{-3} mol L⁻¹, and 1.00×10^{-4} mol L⁻¹, respectively, which are related via the following acid-base equilibrium:

$$\mathsf{HA} \rightleftharpoons \mathsf{A}^- + \mathsf{H}^+ \qquad \qquad K = \frac{[\mathsf{A}^-][\mathsf{H}^+]}{[\mathsf{HA}]} \tag{1}$$

The optical path length is l in Part A. The density of the solution remains constant upon dilution. It is assumed that the only chemical reaction that occurs is eq (1).

A.1 The absorbance of **X** was A_1 at a wavelength of λ_1 . Then, solution **X** was diluted 10pt to twice its initial volume using hydrochloric acid with pH = 2.500. After the dilution, the absorbance was still A_1 at λ_1 . **Determine** the ratio $\varepsilon_{HA}/\varepsilon_{A^-}$, where ε_{HA} and ε_{A^-} represent the absorption coefficients of HA and A⁻, respectively, at λ_1 .



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Part B

Let us consider the following equilibrium in the gas phase.

$$D \rightleftharpoons 2M$$
 (2)

A gaseous sample of pure D is filled into a cuboid container that has a transparent movable wall with a cross-section of S (see the figure below) at a pressure P, and equilibrium is established while the total pressure is kept at P.

The absorbance of the gas is $A = \varepsilon(n/V)l$, where ε , n, V, and l are the absorption coefficient, amount of the gas in moles, volume of the gas, and optical path length, respectively. It is assumed that all components of the gas mixture behave as ideal gases.



Use the following definitions if necessary.

	Initial state		At equilibrium		
	D	М	D	М	
Partial pressure	Р	0	p_{D}	p_{M}	
Amount in moles	n_0	0	n_{D}	n_{M}	
Volume	V_0		V		

- **B.1** The absorbance of the gas at λ_{B1} measured from direction x ($l = l_x$) was A_{B1} for both at the initial state and after the equilibrium is established. **Determine** the ratio $\varepsilon_D / \varepsilon_M$ at λ_{B1} , where ε_D and ε_M represent the absorption coefficients of D and M, respectively.
- **B.2** The absorbance of the gas at λ_{B2} measured from direction y was A_{B2} for both 6pt at the initial state ($l = l_{y0}$) and after the equilibrium is established ($l = l_y$). **Determine** the ratio $\varepsilon_D / \varepsilon_M$ at λ_{B2} .



A3-1 SGP English (Singapore)

SGP-4 C-3 A-1

Lambert-Beer Law?

Part A

A.1 (10 pt)

(Continued on the next page)



_



A.1 (cont.)
$\varepsilon_{HA}/arepsilon_{A^-}=$

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Part B

B.1 (6 pt)

 $\varepsilon_{\rm D}/\varepsilon_{\rm M} =$





B.2 (6 pt) $\varepsilon_{\rm D}/\varepsilon_{\rm M} =$

SGP-4 C-3 A-4

SGP-4 C-4 C Alphonsus Neo

SGP-4 C-4 C-1



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The Redox Chemistry of Zinc

11 % of the total								
Question	A.1	A.2	B.1	B.2	B.3	B.4	Total	
Points	6	5	4	3	5	9	32	
Score								



Zinc has long been used as alloys for brass and steel materials. The zinc contained in industrial wastewater is separated by precipitation to detoxify the water, and the obtained precipitate is reduced to recover and reuse it as metallic zinc.

Part A

The dissolution equilibrium of zinc hydroxide $Zn(OH)_2(s)$ at 25 °C and the relevant equilibrium constants are given in eq. 1–4.

$$\operatorname{Zn}(\operatorname{OH})_2(\mathbf{s}) \rightleftharpoons \operatorname{Zn}^{2+}(\operatorname{aq}) + 2\operatorname{OH}^-(\operatorname{aq}) \qquad K_{\operatorname{sp}} = 1.74 \times 10^{-17}$$
 (1)

$$\operatorname{Zn}(\operatorname{OH})_2(s) \rightleftharpoons \operatorname{Zn}(\operatorname{OH})_2(\operatorname{aq})$$
 $K_1 = 2.62 \times 10^{-6}$ (2)

$$\operatorname{Zn}(\operatorname{OH})_2(\mathsf{s}) + 2\operatorname{OH}^-(\mathsf{aq}) \rightleftharpoons \operatorname{Zn}(\operatorname{OH})_4^{2-}(\mathsf{aq}) \qquad \qquad K_2 = 6.47 \times 10^{-2} \tag{3}$$

$$H_2O(I) \rightleftharpoons H^+(aq) + OH^-(aq) \qquad K_w = 1.00 \times 10^{-14}$$
(4)



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SGP-4 C-4 Q-2

The solubility, *S*, of zinc (concentration of zinc in a saturated aqueous solution) is given in eq. 5.

$$S = [Zn^{2+}(aq)] + [Zn(OH)_2(aq)] + [Zn(OH)_4^{2-}(aq)]$$
(5)

- **A.1** When the equilibria in eq. 1–4 are established, <u>calculate</u> the pH range 6pt in which $[Zn(OH)_2(aq)]$ is the greatest among $[Zn^{2+}(aq)]$, $[Zn(OH)_2(aq)]$ and $[Zn(OH)_4^{2-}(aq)]$.
- **A.2** A saturated aqueous solution of $Zn(OH)_2(s)$ at pH = 7.00 was prepared and filtered. Subsequently, NaOH was added to this filtrate to increase its pH to 12.00. <u>**Calculate</u>** the molar percentage of zinc that precipitates when increasing the pH from 7.00 to 12.00. You may assume that the volume of the solution and temperature remain constant.</u>

Part B

Next, the recovered zinc hydroxide is heated to obtain zinc oxide according to the reaction below:

$$Zn(OH)_2(s) \rightarrow ZnO(s) + H_2O(I)$$
(6)

The zinc oxide is then reduced to metallic zinc by reacting with hydrogen:

$$ZnO(s) + H_2(g) \rightarrow Zn(s) + H_2O(g)$$
(7)

B.1 It is necessary to reduce the partial pressure of the water vapour formed, so 4pt reaction (7) can proceed at a constant hydrogen pressure of 1 bar. <u>**Calculate**</u> the upper limit for the partial pressure of water vapour to allow reaction (7) to proceed at 300 °C. The Gibbs formation energies of zinc oxide and water vapor at 300 °C and 1 bar for all gaseous species are $\Delta G_{ZnO}(300^{\circ}C) = -2.90 \times 10^2 \text{ kJ mol}^{-1}$ and $\Delta G_{H_2O}(300^{\circ}C) = -2.20 \times 10^2 \text{ kJ mol}^{-1}$, respectively.

Metallic zinc is used as a negative electrode (anode) for metal-air batteries. The electrode consists of Zn and ZnO. It uses the following redox reaction to generate electricity with the electromotive force (e.m.f.) at 25 °C and pressure of 1 bar, E° .

$$\operatorname{Zn}(s) + \frac{1}{2}O_2(g) \rightarrow \operatorname{ZnO}(s)$$
 $E^\circ = 1.65 \,\mathrm{V}$ (8)

B.2 A zinc–air battery was discharged at 20 mA for 24 hours. <u>Calculate</u> the change 3pt in mass of the negative electrode (anode) of the battery.






Mt. Fuji

B.3 The e.m.f. of a zinc–air battery is environment dependent. 5pt <u>Calculate</u> the e.m.f. at the summit of Mt. Fuji, where the temperature and altitude are -38 °C (February) and 3776 m, respectively. The atmospheric pressure is represented by

$$P\left[\mathsf{bar}\right] = 1.013 \times \left(1 - \frac{0.0065h}{T + 0.0065h + 273.15}\right)^{5.257} \tag{9}$$

at altitude h [m] and temperature T [°C]. The molar ratio of oxygen in the atmosphere is 21%. The Gibbs energy change of reaction (8) is $\Delta G_{ZnO}(-38^{\circ}C) = -3.26 \times 10^2 \text{ kJ mol}^{-1}$ at $-38^{\circ}C$ and 1 bar.

B.4 The standard reduction potentials, $E^{\circ}(Zn/Zn^{2+})$ and $E^{\circ}(O_2/H_2O)$ at 25 °C and 1 9pt bar are given as (10) and (11), respectively. <u>Calculate</u> the Gibbs energy change for reaction (6) at 25 °C.

 $Zn^{2+} + 2e^- \rightarrow Zn$ $E^{\circ}(Zn^{2+}/Zn) = -0.77 V$ (10)

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$$
 $E^{\circ}(O_2/H_2O) = 1.23V$ (11)



SGP English (Singapore)

The Redox Chemistry of Zinc

SGP-4 C-4 A-1

Part A

A.1 (6 pt)

< pH <





A.2 (5 pt)		
%		





Part B

B.1 (4 pt)			
$p_{H_2O=}$	bar		
<u>PH2O=</u>	bar	 	
<u>P_{H2}O=</u> B.2 (3 pt)	bar	 	
<u>P_{H2}O=</u> B.2 (3 pt)	bar	 	
<u>P_{H2}O=</u> B.2 (3 pt)	<u>bar</u>		
<u>P_{H2}O=</u> B.2 (3 pt)	<u>bar</u>	 	
<u>Р_{H2}O=</u> В.2 (3 pt)	bar		
<u>Рн₂O=</u> В.2 (3 pt)	bar		
<u>Рн₂O=</u> В.2 (3 pt)	bar		
<u>Рн₂O=</u> В.2 (3 pt)	bar		
<u>Рн₂O=</u> В.2 (3 pt)	bar		





B.3 (5 pt)	
V	





B.4 (9 pt)

 $\Delta G^{\circ} = \qquad \qquad {\rm J}\,{\rm mol}^{-1}$

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SGP-4 C-5 C-1



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Mysterious Silicon

12 % of the total								
Question	Question A.1 A.2 A.3 A.4 B.1 B.2 B.3 To							
Points	9	7	6	10	5	15	8	60
Score								



Although silicon is also a group 14 element like carbon, their properties differ significantly.

Part A

Unlike the carbon–carbon triple bond, the silicon–silicon triple bond in a compound formulated as $R^1-Si \equiv Si-R^1$ (R: organic substituent) is extremely reactive. For example, it reacts with ethylene to form a cyclic product that contains a four-membered ring.



When $R^1-Si \equiv Si-R^1$ is treated with an alkyne ($R^2-C \equiv C-R^2$), the four-membered-ring compound **A** is formed as an initial intermediate. Further reaction of another molecule of $R^2-C \equiv C-R^2$ with **A** affords isomers **B** and **C**, both of which have benzene-like cyclic conjugated structures, so-called 'disilabenzenes' that contain a six-membered ring and can be formulated as $(R^1-Si)_2(R^2-C)_4$.





$R^1-Si\equiv Si-R^1 + R^2-C\equiv C-R^2 \longrightarrow A \xrightarrow{R^2-C\equiv C-R^2} B + C$

The ¹³C NMR analysis of the corresponding Si_2C_4 six-membered ring skeletons shows two signals for **B** and one signal for **C**.

- **A.1 <u>Draw</u> the structural formulae of A**, **B**, and **C** using R¹, R², Si, and C. You only 9pt need to provide one of the possible resonance structures.
- **A.2** The enthalpy change in some hydrogenation reactions of unsaturated systems 7pt is shown below (Fig. 1). <u>**Calculate**</u> the aromatic stabilization energy (ASE) for benzene and **C** (for $R^1 = R^2 = H$) as positive values.





When a xylene solution of \mathbf{C} is heated, it undergoes isomerization to give an equilibrium mixture of compounds **D** and **E**. The molar ratio is **D** : **E** = 1 : 40.0 at 50.0 °C and **D** : **E** = 1 : 20.0 at 120.0 °C.

A.3 **Calculate** ΔH for the transformation of **D** to **E**. It is assumed that ΔH is tem-6pt perature independent.

The isomerization from **C** to **D** and to **E** proceeds via transformations of π -bonds into σ -bonds without breaking any σ -bonds. A ¹³C NMR analysis revealed one signal for the Si₂C₄ skeleton of **D** and two signals for that of **E**. The skeleton of **D** does not contain any three-membered rings, while **E** has two threemembered rings that share an edge.

A.4 **Draw** the structural formulae of **D** and **E** using R¹, R², Si, and C.

Part B

Silicon is able to form highly coordinated compounds (> four substituents) with electronegative elements such as fluorine. As metal fluorides are often used as fluorination reagents, highly coordinated silicon fluorides also act as fluorination reagents.

The fluorination reaction of CCl₄ using Na₂SiF₆ was carried out as follows.

• Standardization of Na₂SiF₆ solution :

Preparation

Aqueous solution **F**: 0.855 g of Na₂SiF₆ (188.053 g mol⁻¹) dissolved in water (total volume: 200 mL).

Aqueous solution **G**: 6.86 g of $Ce_2(SO_4)_3$ (568.424 g mol⁻¹) dissolved in water (total volume: 200 mL).

Procedure

The precipitation titration of a solution **F** (50.0 mL) is performed by adding dropwise of solution **G** in the presence of xylenol orange, which as an indicator coordinates to Ce³⁺. After adding 18.8 mL of solution \mathbf{G} , the color of the solution changes from yellow to magenta. The generated precipitate is a binary compound that contains Ce^{3+} , and the only resulting silicon compound is $Si(OH)_4$.

<u>Write</u> the balanced equation for the reaction of Na_2SiF_6 with $Ce_2(SO_4)_3$. **B.1** 5pt

10pt

• Reaction of CCl₄ with Na₂SiF₆:

(Substance losses by *e.g.* evaporation are negligible during the following operations.)

 $Na_2SiF_6(x [q])$ was added to CCl_4 (500.0 q) and heated to 300°C in a sealed pressure-resistant reaction vessel. The unreacted Na₂SiF₆ and the generated NaCl were removed by filtration. The filtrate was subsequently diluted to a total volume of 1.00 L with CCl_4 (solution **H**). The ²⁹Si and ¹⁹F NMR spectra of solution **H** showed SiF₄ as the only silicon containing compound. In the ¹⁹F NMR spectrum, in addition to SiF₄, signals corresponding to CFCl₃, CF₂Cl₂, CF₃Cl, and CF₄ were observed (*cf.* Table 1). The integration ratios in the ¹⁹F NMR spectrum are proportional to the number of fluorine nuclei.

Table 1						
¹⁹ F NMR data	CFCl ₃	CF ₂ Cl ₂	CF₃Cl	CF ₄		
Integration ratio	45.0	65.0	18.0	2.0		



 SiF_4 is hydrolyzed to form H_2SiF_6 according to the following eq. 8:

$$3SiF_4 + 2H_2O \rightarrow SiO_2 + 2H_2SiF_6 \tag{8}$$

Solution **H** (10 mL) was added to an excess amount of water, which resulted in the complete hydrolysis of SiF₄. After separation, the H_2SiF_6 generated from the hydrolysis in the aqueous solution was neutralized and completely converted to Na_2SiF_6 (aqueous solution **J**).

The precipitate of unreacted Na_2SiF_6 and NaCl, which was removed by filtration in the initial step (underlined), was completely dissolved in water to give an aqueous solution (solution **K**; 10.0 L).

Then, additional precipitation titrations using solution **G** were carried out, and the endpoints of the titrations with **G** were as follows:

•For solution **J** (entire amount): 61.6 mL.

•For 100 mL of solution **K**: 44.4 mL.

It should be noted here that the coexistence of NaCl or SiO₂ has no effect on the precipitation titration.

- **B.2** <u>**Calculate**</u> the mass of the NaCl produced in the reaction vessel (information 15pt underlined), and <u>**calculate**</u> the mass (x [g]) of the Na₂SiF₆ used as a starting material.
- **B.3** 77.8% of the CCl_4 that was used as a starting material remained unreacted. 8pt <u>Calculate</u> the mass of CF_3Cl generated.



A5-1 SGP English (Singapore)

SGP-4 C-5 A-1

Mysterious Silicon

Part A

A.1 (9 pt)

A (3 pt)	B (3 pt)	C (3 pt)

A.2 (7 pt)

 $\label{eq:c6} \frac{{\sf C}_6{\sf H}_6: \qquad \ \ \, \ \, kJ\,mol^{-1}, {\sf C}: \qquad \ \ \, kJ\,mol^{-1}}{}$





A.3 (6 pt)			
$\Delta H =$	kJ mol ⁻¹		
A.4 (10 pt))		
	D (5 pt)	E (5 pt)	





Part B

B.1 (5 pt)

B.2 (15 pt)

(Continued on the next page)





B.2 (cont.)		
NaCl :	$g,Na_2SiF_6:$	g





B.3 (8 pt)

 $CF_3CI:$ g

SGP-4 C-6 C Alphonsus Neo

SGP-4 C-6 C-1



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The Solid-State Chemistry of Transition Metals

	13 % of the total										
Question	A.1	A.2	A.3	B.1	B.2	B.3	B.4	C.1	C.2	C.3	Total
Points	6	3	3	6	4	4	4	5	5	5	45
Score											



Volcano at Sakurajima island

Part A

Japan is one of the countries with the highest numbers of volcanos worldwide. When silicate minerals crystallize from magma, a part of the transition-metal ions (M^{n+}) in the magma is incorporated into the silicate minerals. The M^{n+} studied in the problem are coordinated by oxide ions (O^{2-}) and adopt a four-coordinate tetrahedral (T_d) geometry in the magma and six-coordinate octahedral (O_h) geometry in the silicate minerals, both of which exhibit a high-spin electron configuration.

The distribution coefficient of Mⁿ⁺ between the silicate minerals and magma, *D*, can be expressed by:

$$D = \frac{[M]_s}{[M]_1}$$

where $[M]_s$ and $[M]_l$ are the concentrations of M^{n+} in the silicate minerals and the magma, respectively. The table below shows the D values of Cr^{2+} and Mn^{2+} as examples.

	Cr ²⁺	Mn ²⁺
D	7.2	1.1



Let Δ_0 and CFSE⁰ be the energy separation of the d-orbitals of Mⁿ⁺ and the crystal-field stabilization energy in a O_h field, respectively. Similarly, Δ_T and CFSE^T correspond to the energy separation of the d-orbitals of Mⁿ⁺ and the crystal-field stabilization energy in a T_d field, respectively.

- **A.1** <u>**Calculate**</u> $|CFSE^O CFSE^T| = \Delta CFSE$ in terms of Δ_O for Cr^{2+} , Mn^{2+} , and Co^{2+} ; 6pt you may assume $\Delta_T = 4/9\Delta_O$.
- A linear relationship can be obtained by plotting $\ln D$ against $\Delta CFSE / \Delta_0$ in the A.2 3pt Cartesian coordinate system shown below. **Estimate** D for Co²⁺. 2.0 1.5 0.5 0 0 0.1 0.2 0.3 0.4 0.5 $\Delta CFSE / \Delta_{O}$

Metal oxides MO (M: Ca, Ti, V, Mn, or Co) crystallize in a rock-salt structure where the M^{n+} adopts an O_h geometry with a high-spin electron configuration. The lattice enthalpy of these oxides is mainly governed by the Coulomb interactions based on the radius and charge of the ions and some contributions from the CFSE of M^{n+} in the O_h field.

	CaO	TiO	VO	MnO	CoO
(a)	3460	3878	3913	3810	3916
(b)	3460	3916	3878	3810	3913
(c)	3460	3913	3916	3810	3878
(d)	3810	3878	3913	3460	3916
(e)	3810	3916	3878	3460	3913
(f)	3810	3913	3916	3460	3878





Part B

A mixed oxide **A**, which contains La^{3+} and Cu^{2+} , crystallizes in a tetragonal unit cell as shown in Fig.1.

In the $[CuO_6]$ octahedron, the Cu–O length along the *z*-axis (l_z) is longer than that of the *x*-axis (l_x), and $[CuO_6]$ is distorted from the regular O_h geometry. This distortion removes the degeneracy of the e_g orbitals ($d_{x^2-y^2}$ and d_{z^2}).



Fig. 1

A can be synthesized by thermal decomposition (pyrolysis) of complex **B**, which is formed by mixing metal chlorides in dilute aqueous ammonia solution containing squaric acid $C_4H_2O_4$ (a diacid). The pyrolysis behavior of **B** in dry air shows a weight loss of 29.1% up to 200 °C due to the loss of crystallization water, followed by another weight loss up to 700 °C due to the release of CO_2 . The total weight loss during the formation of **A** from **B** is 63.6%. It should be noted that only water and CO_2 are released in the pyrolysis reaction.

B.1	<u>Write</u> the chemical formulae for A and B .	6pt
B.2	Use Fig. 1 to <u>calculate</u> l_x and l_z .	4pt
B.3	For Cu^{2+} in the distorted $[CuO_6]$ octahedron in A of Fig. 1, <u>write</u> the names of the split e_g orbitals $(d_{x^2-y^2}$ and $d_{z^2})$ in (i) and (ii), and <u>draw</u> the electron configuration in the dotted box in your answer sheet.	4pt





A is an insulator. When one La³⁺ is substituted with one Sr²⁺, one hole is generated in the crystal lattice that can conduct electricity. As a result, the Sr²⁺-doped **A** shows superconductivity below 38 K. When a substitution reaction took place for **A**, 2.05×10^{27} holes m⁻³ were generated.

B.4 Calculate the percentage of Sr²⁺ substituted for La³⁺ based on the mole ratio 4pt in the substitution reaction. Note that the valences of the constituent ions and the crystal structure are not altered by the substitution reaction.

Part C

 $Cu_2(CH_3CO_2)_4$ is composed of four $CH_3CO_2^-$ coordinated to two Cu^{2+} (Fig. 2A). $Cu_2(CH_3CO_2)_4$ exhibits high levels of structural symmetry, with two axes passing through the carbon atoms of the four $CH_3CO_2^-$ and an axis passing through the two Cu^{2+} , all of which are oriented orthogonal relative to each other.

When a dicarboxylate ligand is used instead of $CH_3CO_2^{-}$, a "cage complex" is formed. The cage complex $Cu_4(L1)_4$ is composed of planar dicarboxylate L1 (Fig. 2B) and Cu^{2+} (Fig. 2C). The angle θ between the coordination directions of the two carboxylates, indicated by the arrows in Fig. 2B, determines the structure of the cage complex. The θ is 0° for L1. Note that the hydrogen atoms are not shown in Fig. 2.



Fig. 2









A zinc complex, $Zn_4O(CH_3CO_2)_6$, contains four tetrahedral Zn^{2+} , six $CH_3CO_2^{-}$, and one O^{2-} (Fig. 3A). In $Zn_4O(CH_3CO_2)_6$, the O^{2-} is located at the origin, and the three axes passing through the carbon atoms of $CH_3CO_2^{-}$ are oriented orthogonal relative to each other.

When *p*-benzenedicarboxylate (Fig. 3B, **L3**, θ = 180°) is used instead of CH₃CO₂⁻, the Zn²⁺ clusters are linked to each other to form a crystalline solid (**X**) that is called a "porous coordination polymer" (Fig. 3C).

The composition of **X** is $[Zn_4O(L3)_3]_n$, and it has a cubic crystal structure with nano-sized pores. One pore is represented as a sphere in Fig. 3D, and each tetrahedral Zn^{2+} is represented as dark gray polyhedron in Fig. 3C and 3D. Note that the hydrogen atoms are not shown in Fig. 3.



- **C.2 X** has a cubic unit cell with a side length of *a* (Fig. 3C) and a density of 0.592 5pt $g \text{ cm}^{-3}$. **Calculate** *a* in [cm].
- C.3X contains a considerable number of pores, and 1 g of X can accommodate5pt 3.0×10^2 mL of CO2 gas in the pores at 1 bar and 25 °C.CalculateCalculatethe average number of CO2 molecules per pore.





The Solid-State Chemistry of Transition Metals

Part A				
A.1 (6 pt)				
<u>Cr^{2+}</u> :	Δ ₀ , <u>Mn²⁺ :</u>	Δ ₀ , <u>Co²⁺ :</u>	Δ_Ο	











Part B

B.1 (6 pt)		
<u>A</u> :	, <u>B</u> :	
B.2 (4 pt)		











Part C

C.1 (5 pt)		
<u>n</u> =	, <u>m</u> =	-

 $\textbf{C.2}~(5~\mathrm{pt})$

 $\underline{a} =$

cm





C.3 (5 pt)

SGP-4 C-7 C Alphonsus Neo

SGP-4 C-7 C-1



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Playing with Non-benzenoid Aromaticity

13 % of the total					
Question	A.1	A.2	A.3	B.1	Total
Points	5	2	19	10	36
Score					

Prof. Nozoe (1902–1996) opened the research field of non-benzenoid aromatic compounds, which are now ubiquitous in organic chemistry.



Photo courtesy: Tohoku Univ.

Part A

Lineariifolianone is a natural product with a unique structure, which was isolated from *Inula linariifolia*. From valencene (1), a one-step conversion yields **2**, before a three-step conversion via **3** yields ketone **4**. Eremophilene (**5**) is converted into **6** by performing the same four-step conversion.







SGP-4 C-7 Q-2

Inula linariifolia



A.1 Draw the structures of **2** and **6** and clearly identify the stereochemistry where 5pt necessary.

Then, ketone **4** is converted into ester **15**. Compound **8** (molecular weight: 188) retains all the stereocenters in **7**. Compounds **9** and **10** have five stereocenters and no carbon-carbon double bonds. Assume



that $H_2^{18}O$ is used instead of $H_2^{16}O$ for the synthesis of ¹⁸O-labelled-lineariifolianones **13** and **14** from **11** and **12**, respectively. Compounds **13** and **14** are ¹⁸O-labelled isotopomers. Ignoring isotopic labelling, both **13** and **14** provide the same product **15** with identical stereochemistry.











Part B

Compound **19** is synthesized as shown below. In relation to non-benzenoid aromaticity, **19** can be used as an activator for alcohols, and **20** was converted to **22** via ion-pair intermediate **21**. Although the formation of **21** was observed by NMR, **21** gradually decomposes to give **18** and **22**.



B.1 Draw the structures of **17–19** and **21**. Identifying the stereochemistry is not 10pt necessary.



SGP English (Singapore)

Playing with Non-benzenoid Aromaticity

Part A

2 (2 pt)	6 (3 pt)	

SGP-4 C-7 A-1

A.2 (2 pt)




SGP-4 C-7 A-2







SGP-4 C-7 A-3

Part B

17 (2 pt)	18 (2 pt)	
19 (3 pt)	21 (3 pt)	

SGP-4 C-8 C Alphonsus Neo

SGP-4 C-8 C-1



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Dynamic Organic Molecules and Their Chirality

11 % of the total						
Question	A.1	A.2	A.3	B.1	B.2	Total
Points	9	3	7	3	4	26
Score						

Part A

Polycyclic aromatic hydrocarbons with successive ortho-connections are called [n]carbohelicenes (here, n represents the number of six-membered rings) (see below). [4]Carbohelicene ([4]C) is efficiently prepared by a route using a photoreaction as shown below, via an intermediate (Int.) that is readily oxidized by iodine.



The photoreaction proceeds in a manner similar to the following example.





Note: For all of Question 8, please draw alternating single and double bonds in your answers to the problems as depicted in the examples of carbohelicene. Do not use circles for conjugated π systems.

A.1	Draw the structures of A–C . Stereoisomers should be distinguished.	9pt
A.2	Attempts to synthesize [5]carbohelicene from the same phosphonium salt and an appropriate starting compound resulted in the formation of only a trace amount of [5]carbohelicene. Instead, product D , whose molecular weight was 2 Da lower than that of [5]carbohelicene, was obtained. The ¹ H NMR chemical shifts of D are listed below. <u>Draw</u> the structure of D . [D (δ , ppm in CS ₂ , r.t.), 8.85 (2H), 8.23 (2H), 8.07 (2H), 8.01 (2H), 7.97 (2H), 7.91 (2H)]	3pt

[5]- and larger [n]carbohelicenes have helical chirality and interconversion between enantiomers of these helicenes is significantly slow at room temperature. The chirality of [n]carbohelicenes is defined as (*M*) or (*P*) as shown below.



[n]Carbohelicenes with n larger than 4 can be enantiomerically separated by a chiral column chromatography, which was developed by Prof. Yoshio Okamoto.



Photo courtesy: The Japan Prize Foundation



Multiple helicenes are molecules that contain two or more helicene-like structures. If its helical chirality is considered, several stereoisomers exist in a multiple helicene. For example, compound **E** contains three [5]carbohelicene-like moieties in one molecule. One of the stereoisomers is described as (P, P, P) as shown below.



A.3 The nickel-mediated trimerization of 1,2-dibromobenzene generates triphenylene. When the same reaction is applied to an enantiomer of \mathbf{F} , (*P*)- \mathbf{F} , multiple helicene \mathbf{G} ($C_{66}H_{36}$) is obtained. Given that interconversion between stereoisomers does not occur during the reaction, **identify all** the possible stereoisomers of \mathbf{G} formed in this process, without duplication. In the answer, one isomer should be drawn completely with the chirality defined as in the example above, with numerical labels; the other stereoisomers should be listed with location numbers and *M* and *P* labels according to the same numbering. For instance, the other stereoisomers of \mathbf{E} should be listed as (1, 2, 3) = (*P*, *M*, *P*), (*P*, *M*, *M*), (*P*, *P*, *M*), (*M*, *M*, *M*), (*M*, *P*, *P*), and (*M*, *P*, *M*).







Part B

Sumanene is a bowl-shaped hydrocarbon that was first reported in Japan in 2003. The name "sumanene" derives from a Sanskrit-Hindi word "suman" that means sunflower. The synthesis of sumanene was achieved by a reaction sequence that consists of a ring-opening and a ring-closing metathesis.



Representative metathesis reactions catalyzed by a ruthenium catalyst (Ru*) are shown below.



B.1 Draw the structure of intermediate **I** (its stereochemistry is not required). 3pt



the optically active sumanene derivative **K**. The stereocenters in **J** suffer no inversion during the metathesis reaction. **Draw** the structure of **K** with the appropriate stereochemistry.



A8-1 SGP English (Singapore)

SGP-4 C-8 A-1

Dynamic Organic Molecules and Their Chirality

Part A

A.1 (9 pt)

A (3 pt)	B (3 pt)	C (3 pt)

 $\textbf{A.2}~(3~\mathrm{pt})$





A.3 (7 pt)

SGP-4 C-8 A-2





SGP-4 C-8 A-3

Part B

B.1 (3 pt)

B.2~(4~pt)

SGP-4 C-9 C Alphonsus Neo

SGP-4 C-9 C-1



Please return this cover sheet together with all the related question sheets.





Likes and Dislikes of Capsule

10 % of the total						
Question	A.1	A.2	A.3	A.4	A.5	Total
Points	13	2	2	3	3	23
Score						

Good kids don't do this, but if you unseam a tennis ball, you can disassemble it into two U-shaped pieces.



Based on this idea, compounds **1** and **2** were synthesized as U-shaped molecules with different sizes. Compound **3** was prepared as a comparison of **1** and the encapsulation behavior of these compounds was investigated.







The synthetic route to **2** is shown below. The elemental composition of compound **9**: C; 40.49%, H; 1.70%, and O; 17.98% by mass.







A.1 Draw the structures of **4–9**; the stereochemistry can be neglected. Use "PMB" 13pt as a substituent instead of drawing the whole structure of *p*-methoxybenzyl group shown in the scheme above.

In the mass spectrum of **1**, the ion peak corresponding to its dimer ($\mathbf{1}_2$) was clearly observed, whereas an ion peak for $\mathbf{3}_2$ was not observed in the spectrum of **3**.

In the ¹H NMR spectra of a solution of 1_2 , all the NH protons derived from **1** were observed to be chemically equivalent, and their chemical shift was significantly different from that of the NH protons of **3**. These data indicate that hydrogen bonds are formed between the NH moieties of **1** and atoms **X** of another molecule of **1** to form the dimeric capsule.

A.2	<u>Circle</u> all the appropriate atom(s) X in 1 .	2pt
A.3	<u>Give</u> the number of the hydrogen bonds in the dimeric capsule (1 $_2$).	2pt



The dimeric capsule of $\mathbf{1}$ ($\mathbf{1}_2$) has an internal space wherein an appropriate small molecule Z can be encapsulated. This phenomenon is expressed by the following equation:

$$\mathsf{Z} + \mathbf{1}_2 \to \mathsf{Z} \textcircled{\texttt{0}} \mathbf{1}_2 \tag{1}$$

The equilibrium constant of the encapsulation of Z into $\mathbf{1}_2$ is given as below:

$$K_{\mathsf{a}} = \frac{[\mathsf{Z} \textcircled{\texttt{a}} \mathsf{1}_2]}{[\mathsf{Z}][\mathsf{1}_2]} \tag{2}$$

Encapsulation of a molecule into a capsule could be monitored by NMR spectroscopy. For example, 1_2 in C₆D₆ gave different signals in the ¹H NMR spectra before and after addition of CH₄.

Compound **2** also forms a rigid and larger dimeric capsule (2_2). The ¹H NMR spectrum of 2_2 was measured in C₆D₆, C₆D₅F, and a C₆D₆/C₆D₅F solvent mixture, with all other conditions being kept constant. The chemical shifts for the H^a proton of **2** in the above solvents are summarized below, and no other signals from the H^a in **2**, except for the listed, were observed. Assume that the interior of the capsule is always filled with the largest possible number of solvent molecules and that each signal corresponds to one species of the filled capsule.



solvent	δ (ppm) of H ^a
C ₆ D ₆	4.60
C ₆ D ₅ F	4.71
C ₆ D ₆ / C ₆ D ₅ F	4.60, 4.71, 4.82

A.4 Determine the number of C_6D_6 and C_6D_5F molecules encapsulated in 2_2 giving 3pt each H^a signal.



¹H NMR measurements in C_6D_6 revealed that 2_2 can incorporate one molecule of 1-adamantanecarboxylic acid (AdA), and the association constants (K_a) which are expressed below were determined for various temperatures.

$$K_{\mathsf{a}} = \frac{[\mathsf{Z}@\mathbf{2}_2]}{[\mathsf{Z}][\mathsf{solvent}@\mathbf{2}_2]} \tag{3}$$

Similarly, the K_a values of CH₄ and $\mathbf{1}_2$ given as eq (2) at various temperatures in C₆D₆ were also determined by ¹H NMR measurements.

The plots of the two association constants (as $\ln K_a$ vs 1/*T*) are shown below.



No C_6D_6 molecule is encapsulated in 1_2 . Referring to the table below: in line **II**, the entropy change (ΔS) is (1) and enthalpy change (ΔH) is (2), indicating that the driving force for the encapsulation in line **II** is (3). Therefore, line **I** corresponds to (4), and line **II** corresponds to (5).

A.5 F	or (1)–(5), <u>cho</u>	oose the correct option (A	or B)	3pt
		A	В	
	(1)	positive	negative	
	(2)	positive	negative	
	(3)	ΔS	ΔH	
	(4)	1_2 and CH_4	2_2 and AdA	
	(5)	1_2 and CH_4	2_2 and AdA	





SGP-4 C-9 A-1

Likes and Dislikes of Capsule

A.1 (13 pt)		
4 (2 pt)	5 (3 pt)	
6 (2 pt)	7 (2 pt)	
8 (2 pt)	9 (2 pt)	





SGP-4 C-9 A-2

A.2 (2 pt)



A.3 (2 pt)

$\textbf{A.4}~(3~\mathrm{pt})$

δ (ppm) of H ^a	numbers of C ₆ D ₆	numbers of C ₆ D ₅ F	
4.60 ppm			
4.71 ppm			
4.82 ppm			

A.5 (3 pt)

(1):	(2):	(3):

<u>(4)</u>: (5):