Preparatory Problems

"Bonding the World with Chemistry"

49th INTERNATIONAL CHEMISTRY OLYMPIAD
Nakhon Pathom, THAILAND
Preface

On behalf of the scientific committee, I am delighted to provide Preparatory Problems for the 49th International Chemistry Olympiad. The aim of these problems is to facilitate the preparation of participants. We intended to prepare problems to cover wide range of challenging topics in modern chemistry that could be solved by applying fundamental chemical principles covered in high school level along with six topics of advanced difficulty. These advanced topics are listed explicitly under “Topics of Advanced Difficulty” and their applications are demonstrated in the tasks. We expect the participants to be familiar with these topics.

The problems listed in this book consisted of 33 theoretical and 5 practical tasks. We hope you find these tasks useful to prepare for the competition. The official solutions are only available to the mentors of each country in May 2017. The Preparatory Problems with Solutions will be published later on our IChO 2017 website. We welcome any comments, corrections or questions about the problems to icho2017@mahidol.ac.th.

We also would like to take this opportunity to welcome you to Thailand. The International Chemistry Olympiad is a venue for scholarly gathering and certainly will keep the participants intellectually intrigued and inspired. We hope you will enjoy not only a challenging chemistry competition but also great and memorable experiences of Thai cultures. We look forward to seeing you in Thailand.

Acknowledgements

I would like to express my deep gratitude to all the authors for their dedication and effort in contributing to the Preparatory Problems as well as the members of the International Steering Committee for valuable comments and suggestions. I also highly appreciate The Institute for the Promotion of Teaching Science and Technology (IPST) in collaboration with the Faculty of Science, Mahidol University, for facilitating meetings for members of Scientific Committee.

Piniti Ratananukul
Chair–Scientific Committee
Bangkok, 31 January 2017
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Task Authors

Chair of Scientific Committee
Piniti Ratananukul

Advisory Committee
Orn-anong Arqueropanyo
Laddawan Pdungsap
Yenchai Somvichian
Sunanta Vibuljan
Prapin Wilairat

Contributing Authors
Pongsaton Amornpitoksuk
Radchada Buntem
Chutima Jiarpinitnun
Kritsana Jitmanee
Tinakorn Kanyanee
Duangjai Nacapricha
Suwat Nanan
Paiboon Ngernmeesri
Pasit Pakawatpanurut
Shuleewan Rajviroongit
Nuanlaor Ratanawimarnwong
Yupaporn Sameenoi
Anchalee Somsook
Panida Surawatanawong
Akapong Suwattanamala
Jonggol Tantirungrotechai
Yuthana Tantirungrotechai
Saowapak Teerasong
Tienthong Thongpanchang
Charnsak Thongsornkleeb

POSN
Chiang Mai University
Mahidol University
POSN
Mahidol University
Mahidol University

Prince of Songkla University
Silpakorn University
Mahidol University
Chiang Mai University
Chiang Mai University
Mahidol University
Khon Kaen University
Kasetsart University
Mahidol University
Mahidol University
Srinakharinwirot University
Burapha University
Ubon Ratchathani University
Mahidol University
Mahidol University
Mahidol University
Mahidol University
Burapha University
Mahidol University
Mahidol University
King Mongkut's Institute of Technology, Ladkrabang
Mahidol University
Chulabhorn Graduate Institute
Constants and Formulae

Avogadro's constant, \( N_A = 6.0221 \times 10^{23} \text{ mol}^{-1} \)
Boltzmann constant, \( k_B = 1.3807 \times 10^{-23} \text{ J K}^{-1} \)
Universal gas constant, \( R = 8.3145 \text{ J K}^{-1} \text{ mol}^{-1} = 0.08205 \text{ atm L K}^{-1} \text{ mol}^{-1} \)
Speed of light, \( c = 2.9979 \times 10^8 \text{ m s}^{-1} \)
Planck's constant, \( h = 6.6261 \times 10^{-34} \text{ J s} \)
Faraday constant, \( F = 9.64853399 \times 10^4 \text{ C} \)
Mass of electron, \( m_e = 9.10938215 \times 10^{-31} \text{ kg} \)
Standard pressure, \( P = 1 \text{ bar} = 10^5 \text{ Pa} \)
Atmospheric pressure, \( P_{\text{atm}} = 1.01325 \times 10^5 \text{ Pa} = 760 \text{ mmHg} = 760 \text{ torr} \)
Zero of the Celsius scale, 273.15 K

1 picometer (pm) = 10^{-12} m; 1 Å = 10^{-10} m; nanometer (nm) = 10^{-9} m
1 eV = 1.6 \times 10^{-19} J
1 amu = 1.66053904 \times 10^{-27} \text{ kg}

Ideal gas equation: \( PV = nRT \)

Enthalpy: \( H = U - PV \)

Gibbs free energy: \( G = H - TS \)
\( \Delta G = \Delta G^\circ + RT \ln Q \)
\( \Delta G^\circ = -RT \ln K = -nF E^\circ_{\text{cell}} \)

Entropy change: \( \Delta S = \frac{q_{\text{rev}}}{T} \), where \( q_{\text{rev}} \) is heat for the reversible process
\( \Delta S = nR \ln \frac{V_2}{V_1} \) (for isothermal expansion of an ideal gas)

Nernst equation: \( E = E^0 + \frac{RT}{nF} \ln \frac{C_{\text{ox}}}{C_{\text{red}}} \)

Energy of a photon: \( E = \frac{hc}{\lambda} \)

Lambert-Beer law: \( A = \log \frac{I_0}{I} = \varepsilon b C \)

Integrated rate law

Zero order \( [A] = [A]_0 - kt \)

First order \( \ln [A] = \ln [A]_0 - kt \)

Second order \( \frac{1}{[A]} = \frac{1}{[A]_0} + kt \)

Arrhenius equation
\( k = A e^{-E_a/RT} \)

Preparatory problems: 49\textsuperscript{th} IChO, Thailand, 2017
<table>
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<th>1A</th>
</tr>
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<td>2</td>
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<td>3</td>
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<td>Na 22.99</td>
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<td>12</td>
<td>Mg 24.31</td>
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<td>13</td>
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<td>14</td>
<td>Si 28.09</td>
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<td>28</td>
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<td>29</td>
<td>Cu 63.55</td>
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<td>30</td>
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<td>31</td>
<td>Ga 69.72</td>
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<tr>
<td>32</td>
<td>Ge 72.61</td>
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<td>33</td>
<td>As 74.92</td>
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<td>35</td>
<td>Br 80.90</td>
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<td>36</td>
<td>Kr 83.80</td>
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<tr>
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<td>38</td>
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<tr>
<td>39</td>
<td>Y 88.91</td>
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<td>40</td>
<td>Zr 91.22</td>
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<tr>
<td>41</td>
<td>Nb 92.91</td>
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<td>42</td>
<td>Mo 95.95</td>
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<td>Tc 99.84</td>
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<td>44</td>
<td>Ru 101.1</td>
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<td>45</td>
<td>Rh 102.9</td>
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<td>46</td>
<td>Pd 106.4</td>
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<tr>
<td>47</td>
<td>Ag 107.9</td>
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<tr>
<td>48</td>
<td>Cd 112.4</td>
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<tr>
<td>49</td>
<td>In 114.8</td>
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<tr>
<td>50</td>
<td>Sn 118.7</td>
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<td>51</td>
<td>Sb 121.8</td>
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<td>52</td>
<td>Te 127.6</td>
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<td>53</td>
<td>I 126.9</td>
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<td>54</td>
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<td>63</td>
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<td>64</td>
<td>Gd 158.9</td>
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<td>65</td>
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<tr>
<td>66</td>
<td>Dy 167.3</td>
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<td>67</td>
<td>Ho 168.9</td>
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<tr>
<td>68</td>
<td>Er 167.5</td>
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<tr>
<td>69</td>
<td>Tm 181.0</td>
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<tr>
<td>70</td>
<td>Yb 173.0</td>
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<tr>
<td>71</td>
<td>Lu 175.0</td>
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<tr>
<td>72</td>
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<td>73</td>
<td>Pa 231.0</td>
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<tr>
<td>74</td>
<td>U 238.0</td>
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<tr>
<td>75</td>
<td>Np 237.0</td>
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<tr>
<td>76</td>
<td>Pu 239.0</td>
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<tr>
<td>77</td>
<td>Am 243.0</td>
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<tr>
<td>78</td>
<td>Cm 247.0</td>
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<tr>
<td>79</td>
<td>Bk 251.0</td>
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<tr>
<td>80</td>
<td>Cf 252.0</td>
</tr>
<tr>
<td>81</td>
<td>Es 253.0</td>
</tr>
<tr>
<td>82</td>
<td>Fm 257.0</td>
</tr>
<tr>
<td>83</td>
<td>Md 258.0</td>
</tr>
<tr>
<td>84</td>
<td>No 259.0</td>
</tr>
<tr>
<td>85</td>
<td>Lr 261.0</td>
</tr>
</tbody>
</table>

Periodic table of elements
### Characteristic $^1$H NMR Chemical Shifts

<table>
<thead>
<tr>
<th>Type of Hydrogen (R=Alkyl, Ar=Aryl)</th>
<th>Chemical Shift (ppm)</th>
<th>Type of Hydrogen (R=Alkyl, Ar=Aryl)</th>
<th>Chemical Shift (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(CH_3)_4$Si</td>
<td>0 (by definition)</td>
<td>RCHSi</td>
<td>1.5-2.5</td>
</tr>
<tr>
<td>RCH$_3$</td>
<td>0.9</td>
<td>RCH=O</td>
<td>9.5-10.1</td>
</tr>
<tr>
<td>RCH$_2$R</td>
<td>1.2-1.4</td>
<td>RCOOH'</td>
<td>10-13</td>
</tr>
<tr>
<td>R$_3$CH</td>
<td>1.4-1.7</td>
<td>RCOCH$_3$</td>
<td>2.1-2.3</td>
</tr>
<tr>
<td>RCH$_2$I</td>
<td>3.2-3.3</td>
<td>RCOCH$_2$R</td>
<td>2.2-2.6</td>
</tr>
<tr>
<td>RCH$_2$Br</td>
<td>3.4-3.5</td>
<td>RCOOCH$_3$</td>
<td>3.7-3.9</td>
</tr>
<tr>
<td>RCH$_2$Cl</td>
<td>3.6-3.8</td>
<td>RCOOCH$_2$R</td>
<td>4.1-4.7</td>
</tr>
<tr>
<td>RCH$_2$F</td>
<td>4.4-4.5</td>
<td>R$_2$C=CRCH$_2$R</td>
<td>1.6-2.6</td>
</tr>
<tr>
<td>RCH$_2$NH$_2$</td>
<td>2.3-2.9</td>
<td>R$_2$C=CH$_2$</td>
<td>4.6-5.0</td>
</tr>
<tr>
<td>RCH$_2$OH</td>
<td>3.4-4.0</td>
<td>R$_2$C=CHR</td>
<td>5.0-5.7</td>
</tr>
<tr>
<td>RCH$_2$OR</td>
<td>3.3-4.0</td>
<td>RC=CH</td>
<td>2.0-3.0</td>
</tr>
<tr>
<td>RCH$_2$CH$_2$OR</td>
<td>1.5-1.6</td>
<td>ArCH$_3$</td>
<td>2.2-2.5</td>
</tr>
<tr>
<td>R$_2$NH</td>
<td>0.5-5.0</td>
<td>ArCH$_2$R</td>
<td>2.3-2.8</td>
</tr>
<tr>
<td>ROH</td>
<td>0.5-6.0</td>
<td>ArH</td>
<td>6.5-8.5</td>
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</tbody>
</table>

### Characteristic $^{13}$C NMR Chemical Shifts

<table>
<thead>
<tr>
<th>Type of Carbon (R=Alkyl, Ar=Aryl)</th>
<th>Chemical Shift (ppm)</th>
<th>Type of Carbon (R=Alkyl, Ar=Aryl)</th>
<th>Chemical Shift (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RCH$_3$</td>
<td>10-25</td>
<td>RC(triplebond) CR</td>
<td>65-85</td>
</tr>
<tr>
<td>RCH$_2$R</td>
<td>20-35</td>
<td>RCH=CHR</td>
<td>120-140</td>
</tr>
<tr>
<td>R$_3$CH</td>
<td>25-35</td>
<td>ArylC</td>
<td>120-140</td>
</tr>
<tr>
<td>RCH$_2$COR</td>
<td>35-50</td>
<td>RCOOR</td>
<td>160-180</td>
</tr>
<tr>
<td>RCH$_2$Br</td>
<td>25-35</td>
<td>RCONR$_2$ (amide)</td>
<td>165-180</td>
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<tr>
<td>RCH$_2$Cl</td>
<td>40-45</td>
<td>RCOOH</td>
<td>175-185</td>
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<td>RCH$_2$NH$_2$</td>
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<td>RCHO</td>
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<td>RCH$_2$OH</td>
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<td>RCOR</td>
<td>200-215</td>
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<tr>
<td>RCH$_2$OR</td>
<td>65-70</td>
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*Adapted from RSC E-learning website.*
# IR Absorption Frequencies Table

<table>
<thead>
<tr>
<th>Functional Group</th>
<th>Type of Vibration</th>
<th>Characteristic Absorptions (cm⁻¹)</th>
<th>Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alcohol</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>O-H</td>
<td>(stretch, H-bonded)</td>
<td>3200-3600</td>
<td>strong, broad</td>
</tr>
<tr>
<td>O-H</td>
<td>(stretch, free)</td>
<td>3500-3700</td>
<td>strong</td>
</tr>
<tr>
<td>C-O</td>
<td>(stretch)</td>
<td>1050-1150</td>
<td>strong</td>
</tr>
<tr>
<td>Alkane</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-C-H</td>
<td>stretch</td>
<td>2850-3000</td>
<td>strong</td>
</tr>
<tr>
<td>-C-H</td>
<td>bending</td>
<td>1350-1480</td>
<td>variable</td>
</tr>
<tr>
<td>Alkene</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>=C-H</td>
<td>stretch</td>
<td>3010-3100</td>
<td>medium</td>
</tr>
<tr>
<td>=C-H</td>
<td>bending</td>
<td>675-1000</td>
<td>strong</td>
</tr>
<tr>
<td>C=C</td>
<td>stretch</td>
<td>1620-1680</td>
<td>variable</td>
</tr>
<tr>
<td>Alkyl Halide</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C-F</td>
<td>stretch</td>
<td>1000-1400</td>
<td>strong</td>
</tr>
<tr>
<td>C-Cl</td>
<td>stretch</td>
<td>600-800</td>
<td>strong</td>
</tr>
<tr>
<td>C-Br</td>
<td>stretch</td>
<td>500-600</td>
<td>strong</td>
</tr>
<tr>
<td>C-I</td>
<td>stretch</td>
<td>500</td>
<td>strong</td>
</tr>
<tr>
<td>Alkyne</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C-H</td>
<td>stretch</td>
<td>3300</td>
<td>strong, sharp</td>
</tr>
<tr>
<td>−C≡C−</td>
<td>stretch</td>
<td>2100-2260</td>
<td>variable, not present in symmetrical alkynes</td>
</tr>
<tr>
<td>Amine</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N-H</td>
<td>stretch</td>
<td>3300-3500</td>
<td>medium (primary amines have two bands; secondary have one band, often very weak)</td>
</tr>
<tr>
<td>C-N</td>
<td>stretch</td>
<td>1080-1360</td>
<td>medium-weak</td>
</tr>
<tr>
<td>N-H</td>
<td>bending</td>
<td>1600</td>
<td>medium</td>
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<tr>
<td>Aromatic</td>
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</tr>
<tr>
<td>C-H</td>
<td>stretch</td>
<td>3000-3100</td>
<td>medium</td>
</tr>
<tr>
<td>C=C</td>
<td>stretch</td>
<td>1400-1600</td>
<td>medium-weak, multiple bands</td>
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<tr>
<td></td>
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Analysis of C-H out-of-plane bending can often distinguish substitution patterns

## Carbonyl

<table>
<thead>
<tr>
<th>Functional Group</th>
<th>Type of Vibration</th>
<th>Characteristic Absorptions (cm⁻¹)</th>
<th>Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>C=O</td>
<td>stretch</td>
<td>1670-1820</td>
<td>strong</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(conjugation moves absorptions to lower wave numbers)</td>
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</tbody>
</table>

## Ether

<table>
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<tr>
<th>Functional Group</th>
<th>Type of Vibration</th>
<th>Characteristic Absorptions (cm⁻¹)</th>
<th>Intensity</th>
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<tbody>
<tr>
<td>C-O</td>
<td>stretch</td>
<td>1000-1300 (1070-1150)</td>
<td>strong</td>
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### IR Absorption Frequencies of Functional Groups Containing a Carbonyl (C=O)

<table>
<thead>
<tr>
<th>Functional Group</th>
<th>Type of Vibration</th>
<th>Characteristic Absorptions (cm(^{-1}))</th>
<th>Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Carbonyl</strong></td>
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</tr>
<tr>
<td>C=O</td>
<td>stretch</td>
<td>1670-1820</td>
<td>strong</td>
</tr>
<tr>
<td>(conjugation moves absorptions to lower wave numbers)</td>
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<td></td>
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<tr>
<td><strong>Acid</strong></td>
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<td>C=O</td>
<td>stretch</td>
<td>1700-1725</td>
<td>strong</td>
</tr>
<tr>
<td>O-H</td>
<td>stretch</td>
<td>2500-3300</td>
<td>strong, very broad</td>
</tr>
<tr>
<td>C-O</td>
<td>stretch</td>
<td>1210-1320</td>
<td>strong</td>
</tr>
<tr>
<td><strong>Aldehyde</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C=O</td>
<td>stretch</td>
<td>1740-1720</td>
<td>strong</td>
</tr>
<tr>
<td>=C-H</td>
<td>stretch</td>
<td>2820-2850 &amp; 2720-2750</td>
<td>medium, two peaks</td>
</tr>
<tr>
<td><strong>Amide</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C=O</td>
<td>stretch</td>
<td>1640-1690</td>
<td>strong</td>
</tr>
<tr>
<td>N-H</td>
<td>stretch</td>
<td>3100-3500</td>
<td>unsubstituted have two bands</td>
</tr>
<tr>
<td>N-H</td>
<td>bending</td>
<td>1550-1640</td>
<td></td>
</tr>
<tr>
<td><strong>Anhydride</strong></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>C=O</td>
<td>stretch</td>
<td>1800-1830 &amp; 1740-1775</td>
<td>two bands</td>
</tr>
<tr>
<td><strong>Ester</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C=O</td>
<td>stretch</td>
<td>1735-1750</td>
<td>strong</td>
</tr>
<tr>
<td>C-O</td>
<td>stretch</td>
<td>1000-1300</td>
<td>two bands or more</td>
</tr>
<tr>
<td><strong>Ketone</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>acyclic</td>
<td>stretch</td>
<td>1705-1725</td>
<td>strong</td>
</tr>
<tr>
<td>cyclic</td>
<td>stretch</td>
<td>3-membered - 1850 4-membered - 1780 5-membered - 1745 6-membered - 1715 7-membered - 1705</td>
<td>strong</td>
</tr>
<tr>
<td>α,β-unsaturated</td>
<td>stretch</td>
<td>1665-1685</td>
<td>strong</td>
</tr>
<tr>
<td>aryl ketone</td>
<td>stretch</td>
<td>1680-1700</td>
<td>strong</td>
</tr>
</tbody>
</table>

Data from [http://www2.ups.edu/faculty/hanson/Spectroscopy/IR/IRfrequencies.html](http://www2.ups.edu/faculty/hanson/Spectroscopy/IR/IRfrequencies.html)
Fields of Advanced Difficulty

**Theoretical**

1. Solid state and coordination chemistry (crystal structures, crystal field theory, and isomerism of inorganic complexes)
2. Thermodynamics (gases, liquid mixing, temperature dependence of equilibrium constant, electromotive force, and Gibbs free energy)
3. Electrochemistry and electrochemical analysis (amperometry and conductometry)
4. Kinetics (adsorption on solid catalyst, Arrhenius equation, and Integrated rate law)
5. Organic chemistry (stereoisomerism, simple stereocontrolled organic transformations, [4+2]-cycloaddition, and [3,3]-sigmatropic rearrangement)
6. Spectroscopy (Students are expected to relate simple organic structures with their $^1$H-NMR, $^{13}$C-NMR, or IR data.)

**Practical**

1. Use of spectrophotometer
2. Basic techniques in organic synthesis (recrystallization and TLC, following the described procedures)

**Notes:**

1. Although a few examples in the preparatory problems are related to biomolecules, students are not expected to cover any biochemistry or carbohydrate chemistry as advanced topics.

2. Students are not required to use Microsoft Excel or any related computer software during the exam.

3. Students are not expected to determine melting points in the exam.
## Task lists

**Theoretical part**

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Part I: Theoretical Tasks

Task 1. Dimerization of Acetic Acid

Ethanoic acid or acetic acid (CH₃COOH) is partially dimerized into dimers in the vapor phase. At a total pressure of 0.200 atm, ethanoic acid is 92.0% dimerized at 298 K. By increasing the temperature to 318 K, the degree of dimerization is lowered, with \( K_p = 37.3 \).

1.1) Calculate the enthalpy and the entropy changes for the reaction, assuming that \( \Delta H^o \) and \( \Delta S^o \) do not vary with temperature.

1.2) Applying the Le Chatelier’s principle, an increase of pressure should (select one correct answer)

○ favor the dimerization.

○ not favor the dimerization.

1.3) Continued from question 1.2, the extent of dimerization (select one correct answer)

○ decreases with increasing the temperature.

○ increases with increasing the temperature.

Task 2. Solubility of Calcite

Calcite is a stable form of calcium carbonate (CaCO₃). The solubility product (\( K_{sp} \)) is decreased with increasing temperature; \( K_{sp} \) are \( 9.50 \times 10^{-9} \) and \( 2.30 \times 10^{-9} \) at 0 °C and 50 °C, respectively. Estimate the enthalpy change for the solubility process of calcite.

Task 3. Expansion of Ideal Gas and Thermodynamics of Liquid Mixing

3.1) A quantity of 0.10 mol of an ideal gas A initially at 22.2 °C is expanded from 0.200 dm³ to 2.42 dm³. Calculate the values of work (\( w \)), heat (\( q \)), internal energy change (\( \Delta U \)), entropy change of the system (\( \Delta S_{sys} \)), entropy change of the surroundings (\( \Delta S_{surr} \)), and total entropy change (\( \Delta S_{univ} \)) if the process is carried out isothermally and irreversibly against an external pressure of 1.00 atm.

3.2) If 3.00 mol of A is condensed into liquid state and is mixed with 5.00 mol of liquid B, calculate the changes in entropy and Gibbs free energy upon such mixing at 25.0 °C. This mixture can be assumed to be ideal.
**Task 4. Vibrational Frequency of a Diatomic Molecule**

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

\[ E_{v} = \left( v + \frac{1}{2} \right) \hbar \nu \quad ; v = 0, 1, 2, \ldots \]

where \( v \) is the vibrational quantum number and \( \nu \) is the vibrational frequency. The vibrational frequency represented by the harmonic oscillator model is

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

where \( k \) is the force constant and \( \mu \) is the reduced mass.

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

4.1) Find the reduced mass of CX in amu.

4.2) What is atom X?

**Task 5. Water-gas-shift Reaction**

In a drive toward cleaner energy production, fuel cell holds great promise because of its capability of generating electricity directly from chemical reactions with environmentally-benign byproducts. In particular, for hydrogen fuel cell, the only waste produced by the device is just water.

In order to use fuel cell at an industrial scale, continuous production of hydrogen that directly feeds into a fuel cell module is required. One option to mass produce hydrogen for this purpose is the conversion of hydrocarbon fuel using hot steam. However, this kind of reaction often leads to mixed products that consist of H\(_2\), CO\(_2\), and CO. Moreover, CO is not only hazardous to human health, but it also degrades fuel cell’s active material. The reversible water-gas-shift (WGS) reaction, CO + H\(_2\)O \( \rightleftharpoons \) CO\(_2\) + H\(_2\), provides one method of converting toxic CO into CO\(_2\) and useful H\(_2\). The efficiency of this reaction strongly depends on the solid catalyst used.

5.1) In one process, an equimolar mixture of CO and steam is continuously passed to a WGS reactor containing catalyst at atmospheric pressure and 0 °C. Assuming that the catalyst is 95.0% efficient in converting the reactants into the products and that the reaction in the reactor is approximately at equilibrium in this condition, estimate the free energy change for this reaction?
5.2) Now assume that a large surface of catalyst is initially available to reacting molecules, and the rate of reaction is measured immediately at the onset of the reaction. Below are the initial rates measured at different initial pressures of CO and H₂O.

<table>
<thead>
<tr>
<th>Trial</th>
<th>$P_{CO}$, atm</th>
<th>$P_{H₂O}$, atm</th>
<th>$\frac{dP_{H₂}}{dt}$, atm s⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.10</td>
<td>0.90</td>
<td>$4.0 \times 10^{-4}$</td>
</tr>
<tr>
<td>2</td>
<td>0.15</td>
<td>0.85</td>
<td>$5.6 \times 10^{-4}$</td>
</tr>
<tr>
<td>3</td>
<td>0.25</td>
<td>0.75</td>
<td>$8.2 \times 10^{-4}$</td>
</tr>
<tr>
<td>4</td>
<td>0.28</td>
<td>0.72</td>
<td>X</td>
</tr>
</tbody>
</table>

What is X?

5.3) In another condition where the pressure of hydrogen is found to be 0.50 atm, $\frac{dP_{H₂}}{dt} = 3.0 \times 10^{-7}$ atm s⁻¹. According to the information given in questions 5.1, 5.2, and this question, estimate the rate of hydrogen production when the pressures in the reactor of CO, H₂O, CO₂, and H₂ are 0.14, 0.14, 0.36, and 0.36 atm, respectively. (Give your answer to three significant figures.)

5.4) Calculate the Gibbs free energy change for the conditions described in question 5.3.

5.5) Surface coverage, $\theta$, is an important kinetics parameter, especially for reactions on solid surfaces. It can be defined as the number of adsorbed molecules on a surface divided by the total number of adsorbing sites on that surface. For WGS, after the adsorption of CO and H₂O on the catalyst’s surface, a carbonyl intermediate can be formed, which then dissociates to give surface-bound CO₂ and H atom. If the carbon dioxide is produced at a rate of $1.0 \times 10^{11}$ molecules s⁻¹ cm⁻² with associated rate constant of $2.0 \times 10^{12}$ molecules s⁻¹ cm⁻², what is the value of $\theta$ for this intermediate?

**Task 6. Camphor in Benzene**

The vapor pressure of pure benzene (C₆H₆) is 100 torr at 26.1 °C. Calculate the vapor pressure and the freezing point of a solution containing 24.6 g of camphor (C₁₀H₁₆O) dissolved in 100 cm³ of benzene. The density of benzene is 0.877 g cm⁻³. The freezing point and the cryoscopic constant ($K_f$) of pure benzene are 5.50 °C and 5.12 °C kg mol⁻¹, respectively.
Task 7. Gas and Liquid

7.1) At temperatures above the boiling point, A behaves like an ideal gas. In a hypothetical situation, Jacques Charles performed an experiment about the volume-temperature relationship and obtained the following result (which is not necessarily drawn to scale):

![Graph showing the relationship between volume and temperature for A]

What is the volume of A at 100 °C?

7.2) At equilibrium, the vapor pressures above liquids B and C are 100.1 kPa and 60.4 kPa, respectively. The two liquids B and C are mixed thoroughly at 298 K. What is the vapor pressure above a mixture containing 3 mol B and 4 mol C?

7.3) What are the mole fractions of B and C above the mixture explained in question 7.2?

Task 8. Decomposition of Nitrous Oxide

Nitrous oxide decomposes exothermically into nitrogen and oxygen, at a temperature of approximately 565 °C.

\[2\text{N}_2\text{O} \rightarrow 2\text{N}_2(\text{g}) + \text{O}_2(\text{g})\]

This reaction follows the second-order kinetics when carried out entirely in the gas phase.

8.1) If the reaction is initiated with [N_2O] equal to 0.108 mol dm\(^{-3}\), what will its concentration be after 1250 s have elapsed at 565 °C? The rate constant for the second order decomposition of N_2O is 1.10 \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} at this temperature.

8.2) The activation energy for the second order reaction at 565 °C is 234 kJ mol\(^{-1}\). What is the rate constant for the reaction at 600 °C?
Task 9. Avogadro’s Number

An internationally accepted procedure is as follows.

We start with a “perfect” sphere of pure $^{28}$Si isotope. The weight of this sphere is $W$ g. The volume $V$ of the sphere is found from the accurate measurement of the diameter of the sphere. The unit cell of a crystal of silicon is a “diamond cubic lattice”, i.e. a face-centered unit cell but with 4 Si atoms inside the cube. The length of the unit cell can be determined precisely from X-ray crystallographic measurements of a single crystal of $^{28}$Si isotope.

The experimental data are as follow:

- Weight of sphere, $W$: 1000.064 543(15) g
- Volume of sphere: 431.049 110(10) cm$^3$
- Length of unit cell, $\alpha$: 543.099 619(20) pm
- Atomic weight of $^{28}$Si, $A$: 27.976 970 029(23) g mol$^{-1}$

Number of Si atoms in unit cell, $n$:

1. Write down the equation for calculating Avogadro’s number $N_A$ in terms of the parameters.

2. How many silicon atoms are in the unit cell?

3. Calculate Avogadro’s number using the above data. Give answer to 7 significant figures.
Task 10. Buffer from Biological Acid: Lysine

Acid Dissociation Constants

10.1)

<table>
<thead>
<tr>
<th>Name</th>
<th>Carboxylic acid pKa</th>
<th>Ammonium pKa</th>
<th>Substituent pKa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lysine</td>
<td>2.16</td>
<td>9.06</td>
<td>10.54</td>
</tr>
</tbody>
</table>

One of essential amino acids, lysine, is normally depicted using the molecular structure below: Note that the amine group on the left is part of the substituent group. Is lysine likely to exist in this form when dissolved in neutral aqueous solution? If not, write the correct form.

\[
\text{H}_2 \text{N} \quad \text{O} \quad \text{OH} \\
\text{NH}_2
\]

10.2) Draw the molecular structures for dominant forms of lysine that are present in aqueous solution and arrange them in order from the most acidic form to the most basic form. Use Na\(^+\) or Cl\(^-\) to balance the charge. Label each structure with the name of the compound.

10.3) To prepare buffer solution, you start with the most acidic form of lysine that has the concentration of 0.100 mol dm\(^{-3}\) with the volume of 100 cm\(^3\). How many cm\(^3\) of 0.500 mol dm\(^{-3}\) KOH should you add to obtain a pH of 9.5?

10.4) Dissolve 5.00 g of the neutral zwitterion form of lysine in 100.0 cm\(^3\) of pure water. Determine pH of the solution once equilibrium is reached.

10.5) Determine the equilibrium concentrations of all other forms of lysine present in the solution prepared in question 10.4.
Task 11. Amperometric Titration: Titration of Pb\(^{2+}\) with Cr\(_2\)O\(_7^{2-}\)

Amperometry is one of the sensitive electroanalytical methods used for quantitative determination of electroactive species. A working electrode is held at a certain voltage (vs reference electrode) that is suitable for oxidation or reduction of an analyte. The analyte will be oxidized or reduced at the surface of the working electrode and the current passing through this electrode is measured. This current is directly proportional to the concentration of analyte and is used for quantitative purpose. It can be used for detection of titration end-point. In this example amperometric detection was used for monitoring a titration progress. 20-cm\(^3\) of lead (II) ion solution was titrated with 0.0020 mol dm\(^{-3}\) potassium dichromate solution. A dropping mercury electrode (DME) was used as a working electrode and the potential of -0.8 V (vs SCE, saturated calomel electrode) was applied to this electrode for enabling the reduction of lead (II) ion and dichromate ion with potassium nitrate as supporting electrolyte. The current-volume of titrant data are shown in Table 1.


Table 1. Titration data

<table>
<thead>
<tr>
<th>Volume of 0.0020 mol dm(^{-3}) dichromate (cm(^3))</th>
<th>Current (microampere)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>9.8</td>
</tr>
<tr>
<td>2.00</td>
<td>8.0</td>
</tr>
<tr>
<td>4.00</td>
<td>6.0</td>
</tr>
<tr>
<td>6.00</td>
<td>4.0</td>
</tr>
<tr>
<td>8.00</td>
<td>2.2</td>
</tr>
<tr>
<td>10.00</td>
<td>3.5</td>
</tr>
<tr>
<td>12.00</td>
<td>5.5</td>
</tr>
<tr>
<td>14.00</td>
<td>7.6</td>
</tr>
<tr>
<td>16.00</td>
<td>9.5</td>
</tr>
</tbody>
</table>

11.1) Plot the titration curve and find the titration end point. (The point where the change in the slope of titration curve occurs)

11.2) Write the titration reaction.

11.3) Calculate the concentration of lead (II).
Task 12. Conductometric Titration

Conductivity detector is an electrochemical technique which applies alternating current (AC) signal to two identical electrodes. The applied AC signal induces ions to move in solution and switching of polarity of the AC voltage avoids electrolytic reaction at the electrode. As a result, the mobility of ions in solution relates to the conductivity of ions in solution. Conductivity probe was used in acid-base titration of 25.00 cm$^3$ HCl vs 0.100 mol dm$^{-3}$ NaOH. The conductivity signal was recorded during NaOH addition. The conductometric titration setup is shown in Fig 1. When standard NaOH solution was dropped under gravity force to the titration cell at 3 drops per second and the conductivity value from conductometer recorded, the plot of conductivity of solution vs titration time is shown in Fig 2.

![Fig 1. Conductometric titration setup.](image1)

![Fig 2. Plot of conductivity of an initial 25.00 cm$^3$ HCl vs titration time.](image2)

12.1) Explain why the slope of titration curve before and after the turning point is different.

12.2) Calculate the concentration of HCl, if the volume of NaOH of each drop is 0.029 cm$^3$ and the turning point is at 108 second.
Task 13. Titration of Cu and Zn in Metal Alloy

A metal alloy which contains mainly Cu and Zn was analyzed for its metal content. An alloy sample of 2.300 g was placed in a 250 cm$^3$ erlenmeyer flask. To this flask, 5.00 cm$^3$ of mixed acid (concentrated nitric acid and concentrated hydrochloric acid) was added in a fume hood for dissolution of the alloy. The resulting solution was transferred quantitatively into 250 cm$^3$ volumetric flask and adjusted to volume with deionized water.

A 25.00 cm$^3$ aliquot of sample solution was adjusted to pH 5.5 and titrated with 0.100 mol dm$^{-3}$ EDTA solution using 1-(2-pyridineazo)-2-naphthol or PAN as indicator. The indicator changed color when 33.40 cm$^3$ 0.100 mol dm$^{-3}$ EDTA was added to the sample solution.

Another 25.00 cm$^3$ aliquot of sample solution was adjusted to neutral pH and mixed with excess KI. The mixture was then filtered and the resulting solution was titrated against 0.100 mol dm$^{-3}$ sodium thiosulfate using starch solution as indicator. The titration required 29.35 cm$^3$ sodium thiosulfate to reach the endpoint. Note: $K_{SP(CuI)} = 1.1 \times 10^{-12}$

13.1) Write the oxidative dissolution reaction(s) of an alloy with nitric acid and hydrochloric acid.

13.2) Determine the %w/w of Cu and Zn in alloy.

Task 14. Spectrophotometric Determination of Iron

To study in vitro gastric digestion of iron, the following procedure is carried out. Dried and homogeneously ground supplement tablet of 0.4215 g is accurately weighed, mixed with 10 cm$^3$ of water, adjusted to pH 2.0 with 6 mol dm$^{-3}$ HCl, 0.375 cm$^3$ of pepsin solution (16% w/v) added, and adjusted to 12.50 cm$^3$ with 0.01 mol dm$^{-3}$ HCl. This mixture was quantitatively transferred into a dialysis bag of a fixed volume, which is further immersed for 2 hours in a 20.00 cm$^3$ solution containing 0.01 mol dm$^{-3}$ HCl. Iron released by gastric digestion is dialyzed until the concentration of iron inside and outside the dialysis bag are equal.
To determine the gastric digestible iron from the supplement tablet, colorimetric measurement after complex formation between ferrous ion (M) and complexing agent (L) is carried out at pH 5.0. The resulting $ML_3$ complex exhibits light absorption at 520 nm, whereas M and L do not absorb light at this particular wavelength. Within the visible wavelength region, ferrous ion (M) does not absorb light, the complex ML absorbs light at $X$ nm with the molar absorptivity of $50 \text{L mol}^{-1} \text{cm}^{-1}$, and the complex $ML_2$ absorbs light at $Y$ nm with the molar absorptivity of $200 \text{L mol}^{-1} \text{cm}^{-1}$.

14.1) The stepwise constants, $K_1$, $K_2$ and $K_3$, refer to the formation of the complexes one step at a time.

(i) At equilibrium, the absorbance of the solution (in 1.0-cm cuvette) at $X$ nm is 0.400. This solution also contains $1 \times 10^{-5}$ mol dm$^{-3}$ of M and $2 \times 10^{-6}$ mol dm$^{-3}$ of L. Calculate the stepwise formation constant of ML ($K_1$).

(ii) Then, L is added into the solution. At equilibrium, the absorbance of the solution (in 1.0-cm cuvette) at $Y$ nm is 0.400. This solution also contains $2 \times 10^{-6}$ mol dm$^{-3}$ of ML and $2 \times 10^{-4}$ mol dm$^{-3}$ of L. Calculate the stepwise formation constant of $ML_2$ ($K_2$).
(iii) In an excess of L, all of iron is in the form of ML₃.

Consider the following table:

<table>
<thead>
<tr>
<th>[M], mol dm⁻³</th>
<th>[L], mol dm⁻³</th>
<th>Abs (at 520 nm), pathlength (b) = 1 cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.25 x 10⁻⁵</td>
<td>2.20 x 10⁻²</td>
<td>0.750</td>
</tr>
<tr>
<td>3.25 x 10⁻⁵</td>
<td>9.25 x 10⁻⁵</td>
<td>0.360</td>
</tr>
</tbody>
</table>

a) Calculate the molar absorptivity (Ɛ) of ML₃ complex

b) Calculate the overall formation constant (Kᵢ) of ML₃ complex

c) Calculate the stepwise formation constant (K₃) of the complex

14.2) The CHN analysis shows that the complexing agent (L) contains 80% C, 4.44% H, and 15.56% N. The molar mass of this compound is 180 g. Determine the molecular formula of L.

14.3) The Fe²⁺ complexes, ML, ML₂ and ML₃, adopt the octahedral structure (assume perfect octahedral geometry for each isomer of these three complexes). Sketch the d-orbital splitting diagram for ML₃. Draw all possible isomers of Fe²⁺ complexes. Order the magnitudes of Δ₀ (crystal field splitting) of these three complexes and explain.(Spectrochemical series: I⁻ < Br⁻ < Cl⁻ ≈ SCN⁻ < F⁻ ≈ urea < ONO₂⁻ < OH⁻ < H₂O < NCS⁻ < pyridine < NH₃ < en < bipy < o-phen < NO₂⁻ < CN⁻ ≈ CO)

14.4) To determine the dialyzable iron concentration (iron outside the dialysis bag), 5.00 cm³ of the solution outside the dialysis bag is added with a reducing agent to ensure that all of dissolved iron is in the ferrous ion form. Then, the solution is adjusted to the suitable pH, followed by addition of excess amount of complexing agent (L) and deionized water added to make up the volume to 50.00 cm³ in a volumetric flask. The absorbance measured at 520 nm is 0.550. Calculate the concentration of dialyzable iron (in unit of mg dm⁻³).

14.5) Presume all of the iron in the supplement tablet is completely digestible in the gastric condition. Determine in mg the iron in 1.0000 g of supplement tablet.
Task 15. Basic Electrochemistry

Consider the following electrochemical cell:

\[ \text{Pt(s)} \mid \text{MnO}_4^- (0.00100 \text{ mol dm}^{-3}), \text{Mn}^{2+}(0.00200 \text{ mol dm}^{-3}), \text{pH}=3.00 \parallel \text{Ce}^{4+}(0.0100 \text{ mol dm}^{-3}), \text{Ce}^{3+}(0.0100 \text{ mol dm}^{-3}) \mid \text{Pt(s)} \]

The relevant reduction half-reactions are:

\[ \text{Ce}^{4+} + e^- \rightarrow \text{Ce}^{3+} \quad E^\circ = 1.70 \text{ V} \]

\[ \text{MnO}_4^- + 8\text{H}^+ + 5e^- \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O} \quad E^\circ = 1.507 \text{ V} \]

15.1) Write a balanced net reaction for this cell and determine the values of \(E^\circ_{\text{cell}}\) and \(K\) for the net reaction.

15.2) How many Coulombs of electron charge are transferred when 5.0 mg of \(\text{Ce}^{4+}\) are consumed in the reaction from question 15.1?

15.3) Determine the cell potential for the electrochemical cell shown in the cell diagram.

Task 16. Calculation of Concentration

16.1) What is the concentration of Cu (in \(\text{mol dm}^{-3}\)) prepared by mixing \(\text{CuCl}_2\) 1.345 g with 50.00 cm\(^3\) of \(\text{CuSO}_4\) 31.9 g \(\text{dm}^{-3}\) and adjusting the volume to 500 cm\(^3\) by 0.01 \(\text{mol dm}^{-3}\) HCl?

16.2) Calculate whether or not a precipitate will form if 25.00 cm\(^3\) aliquot of the resulting solution in 16.1 is adjusted to pH 8.0 with NaOH and the final volume is 100.0 cm\(^3\). Note: \(K_{SP(\text{Cu(OH)}_2)} = 4.8 \times 10^{-20}\)
Task 17. Small Molecule Activation by Frustrated Lewis Pairs

Electron acceptors and electron donors are usually called Lewis acids and Lewis bases, respectively.

17.1) Trispentafluorophenylborane is a well-known Lewis acid for the polymerization of olefin. Propose a reaction to prepare trispentafluorophenylborane from boron trichloride and bromopentafluorobenzene.

17.2) The steric hindrance precludes the formation of classical bonds between Lewis acid and Lewis base. Propose a structure of Frustrated Lewis Pairs from the reaction of B(C₆F₅)₃ and PH(t-Bu)₂ if a zwitterion product is only obtained. (See Reference: Welch, G. C.; Juan, R. R. S.; Masuda, J. D.; Stephan, D. W. Science 2006, 314, 1124-1126.)

17.3) Propose a reaction between the obtained zwitterion in 17.2 and Me₂SiHCl.

17.4) Show the structure of the product obtained from the B(C₆F₅)₃ and P(t-Bu)₃ under hydrogen gas atmosphere.

17.5) If HD is used instead of dihydrogen gas, write down all possible products.

17.6) Only one product is obtained from the reaction of B(C₆F₅)₃ and P(t-Bu)₃ under ethylene gas atmosphere. Draw its structure.

17.7) Draw the structure of the product if the reaction of the isolated product from 17.6 is carried out under nitric oxide gas atmosphere.

17.8) Only one product is obtained from the reaction of B(C₆F₅)₃ and P(t-Bu)₃ under carbon dioxide gas atmosphere. Draw its structure.
**Task 18. Silver Iodide**

The crystalline structure of $\beta$-AgI is similar to that of ice, allowing it to induce freezing by the process known as heterogeneous nucleation (cloud seeding). $\beta$-AgI is a bright yellow solid and has the wurtzite structure.

18.1) When the solid silver iodide is exposed to sunlight, it will darken rapidly. What is the oxidation state of silver in the darkened solid?

18.2) What is the solubility trend in AgF, AgCl, AgBr, AgI?

18.3) Consider:

- (a) $\text{Ag}^+ (aq) + e^- \rightarrow \text{Ag} (s)$  \hspace{1cm} $E^0 = +0.80 \text{ V}$
- (b) $\text{AgI} (s) \leftrightharpoons \text{Ag}^+ (aq) + \text{I}^- (aq)$  \hspace{1cm} $K_{sp} = 8.51 \times 10^{-17}$
- (c) $\text{Ag}^+ (aq) + 3 \text{I}^- (aq) \rightarrow \text{[AgI}_3]^{2-} (aq)$  \hspace{1cm} $K = 10^{14}$

From the given information, find the standard reduction potential of $\text{[AgI}_3]^{2-}$.

18.4) The salt $[\text{PPh}_3\text{Me}]_2[\text{AgI}_3]$ contains a triiodoargentate(I) ion $[\text{AgI}_3]^{2-}$ with approximate trigonal planar geometry. (See reference: Bowmaker, G. A.; Camus, A.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.*, **1990**, 727-731.) The structure of $[\text{AgI}_3]^{2-}$ is shown below. Draw the crystal field splitting diagram for the $d$ orbitals of silver and fill in all appropriate electrons.

![Crystal Field Splitting Diagram](image)
Task 19. Perovskite Structure

A mineral perovskite crystallizes in the cubic unit cell in which Ca$^{2+}$ and O$^{2-}$ ions constitute a ccp arrangement and Ti$^{4+}$ ion occupies an interstitial hole as shown here.

19.1) Based on the unit cell above, what is the empirical formula of perovskite?

19.2) Name types of interstitial holes present in the ccp unit cell. How many holes are there, for each type, within the unit cell?

19.3) From your answer in 19.2, which type of interstitial hole is occupied by Ti$^{4+}$ ion?
**Task 20. Quantum Numbers and Atomic Orbitals**

20.1) Each of the following sets of quantum numbers is not permissible for an orbital. Why?

<table>
<thead>
<tr>
<th></th>
<th>n</th>
<th>l</th>
<th>m_l</th>
<th>m_s</th>
</tr>
</thead>
<tbody>
<tr>
<td>(i)</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>+1/2</td>
</tr>
<tr>
<td>(ii)</td>
<td>3</td>
<td>1</td>
<td>-2</td>
<td>-1/2</td>
</tr>
<tr>
<td>(iii)</td>
<td>2</td>
<td>-1</td>
<td>0</td>
<td>+1/2</td>
</tr>
</tbody>
</table>

20.2) Give the notation for the subshells denoted by the following quantum numbers.

(i) \( n = 6, l = 2 \)

(ii) \( n = 4, l = 3 \)

(iii) \( n = 6, l = 1 \)

20.3) What is the number of different orbitals in each of the following subshells?

(i) \( 3d \)

(ii) \( n = 5, l = 3 \)

(iii) \( n = 3, l = 0 \)
**Task 21. Radioactivity of Iodine and Nuclear Equations**

21.1) The half-life of I-131 is 8 days. If a freshly prepared solution of I-131 has a concentration of 0.1 mol dm\(^{-3}\),

(i) what will be the concentration of I-131 after 2 half-lives?

(ii) what will be the concentration of I-131 after 40 days?

21.2) Identify X in each of the following nuclear equations:

(i) \( X \rightarrow ^{14}_{7}\text{N} + \beta^- \)

(ii) \( ^{38}_{13}\text{K} \rightarrow ^{38}_{18}\text{Ar} + X \)

(iii) \( ^{55}_{26}\text{Fe} + ^0_{-1}\text{e} \rightarrow X \)

(iv) \( X \rightarrow ^{234}_{90}\text{Th} + ^2_{4}\text{He} \)

(v) \( ^{14}_{7}\text{N} + X \rightarrow ^{14}_{6}\text{C} + ^1_{1}\text{H} \)

(vi) \( ^{110m}_{47}\text{Ag} \rightarrow X + \gamma \)

(vii) \( ^1_{0}\text{n} + ^{235}_{92}\text{U} \rightarrow ^{136}_{53}\text{I} + X + 4^1_{0}\text{n} \)

(viii) \( ^2_{1}\text{H} + ^3_{1}\text{H} \rightarrow X + ^1_{0}\text{n} \)

**Task 22. Structure and Chemistry of Sodium Chloride**

22.1) The unit cell of NaCl is shown below:

(i) What is the coordination number of Na\(^+\) and Cl\(^-\)?

(ii) What is the number of formula units in the unit cell?

(iii) If the length of the unit cell of NaCl is 560 pm and the mass of NaCl is 58.5 g mol\(^{-1}\), what is the density of NaCl?
22.2) NaCl can be prepared by a reaction between Na(s) and Cl\(_2\)(g):

\[
\text{Na}(s) + \frac{1}{2}\text{Cl}_2(g) \rightarrow \text{NaCl} \quad \Delta H_{\text{formation}} = -411 \text{ kJ}
\]

(i) What are the values of \(n\) and \(l\) for the valence electrons of a Na atom?

(ii) Compare the size of Na vs. Cl and Na\(^+\) vs. Cl\(^-\).

(iii) Draw the Lewis structure of Cl\(_2\).

(iv) Calculate the lattice energy of NaCl.

where \(\Delta H_{\text{sublimation}}\) for Na = 107 kJ mol\(^{-1}\), \(IE_1\) for Na = 496 kJ mol\(^{-1}\), Cl–Cl dissociation = 244 kJ mol\(^{-1}\), Electron Affinity of Cl = -349 kJ mol\(^{-1}\)

22.3) Chemistry of NaCl:

(i) Write the reaction between NaCl(\(aq\)) and Br\(_2\)(\(l\)).

(ii) Write the ionic equation between NaCl(\(aq\)) and AgNO\(_3\)(\(aq\)).

(iii) What is the flame color when NaCl is placed in the flame?
**Task 23. Natural Chelator from Shrimp Shell**

Chitosan is a linear polysaccharide composed of β-(1-4)-linked D-glucosamine (deacetylated unit) and N-acetyl-D-glucosamine (acetylated unit). It is made by treating the chitin shells of shrimp or other crustaceans with a strong base, like sodium hydroxide. The deacetylation of chitin by a strong base yields partially-acetylated chitosan as shown below:

Chitosan can be used for a variety of purposes like helping plants to fight off fungal infections, preventing spoilage in wine, helping deliver drugs through the skin, being applied to reduce bleeding, and as an antibacterial agent. In the environmental aspect, chitosan can be used as an effective metal ion adsorbent. The adsorption capacities of chitosan for Cu(II), Hg(II), Pb(II) and Zn(II) are 79.94, 109.55, 37.2, 47.15 mg (g chitosan)^{-1}, respectively.

23.1) Suggest the preferred binding sites in completely-deacetylated chitosan for metal ion.

The selectivity of chitosan towards Pb^{2+} can be increased by modification with CS_{2} yielding partially modified chitosan (PMCS) as in the structure below:
The absorption capacity toward Pb\(^{2+}\) was increased from 37.2 to 156.0 mg g\(^{-1}\) chitosan (Wang, N.; Zheng, P.; Ma, X. Powder Technol. 2016, 301, 1-9.)

23.2) Suggest the most preferred site(s) in chitosan for Pb\(^{2+}\) and draw the bond(s) between that preferred site(s) and Pb\(^{2+}\). Explain the increase in absorption capacity of PMCS toward Pb\(^{2+}\).

To increase the sensitivity of the chitosan toward metal ion, the dye like meso-tetra(p-carboxyphenyl)porphyrin is chemically bonded with chitosan matrix. After the two acidic protons are removed, the four nitrogen atoms will bind with metal ion. The two axial sites of the metal ion normally bind with water molecules yielding the octahedral complex. Each metal ion gives characteristic absorption maximum in the visible range.

23.3) Suggest the bonds between meso-tetra(p-carboxyphenyl)porphyrin and chitosan if a weak protonic acid is used as a catalyst.

23.4) If Fe\(^{2+}\) is being adsorbed by the chitosan-porphyrin adsorbent, draw the structure of the complex and predict the approximate d-orbital splitting in the proposed complex.
**Task 24. Compound Identification and Related Chemistry**

A reaction between M and Cl₂ gives the only product \( M_x Cl_y \). The following results are obtained under various conditions:

<table>
<thead>
<tr>
<th>M (mol)</th>
<th>Cl₂ (mol)</th>
<th>Product (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.20</td>
<td>0.80</td>
<td>26.7</td>
</tr>
<tr>
<td>0.30</td>
<td>0.70</td>
<td>40.0</td>
</tr>
<tr>
<td>0.40</td>
<td>0.60</td>
<td>53.3</td>
</tr>
<tr>
<td>0.50</td>
<td>0.50</td>
<td>44.4</td>
</tr>
<tr>
<td>0.60</td>
<td>0.40</td>
<td>35.6</td>
</tr>
<tr>
<td>0.70</td>
<td>0.30</td>
<td>26.7</td>
</tr>
<tr>
<td>0.80</td>
<td>0.20</td>
<td>17.8</td>
</tr>
</tbody>
</table>

24.1) What is the chemical formula of \( M_x Cl_y \)? Identify M.

24.2) Write balanced chemical equations of:
   
   (i) complete hydrolysis of \( M_x Cl_y \)
   
   (ii) \( M_x Cl_y + H_2SO_4 \)

24.3) At certain temperatures, \( M_x Cl_y \) exists in equilibrium as a dimer:

\[
M_x Cl_y \quad \rightleftharpoons \quad (M_x Cl_y)_2
\]

Draw a chemical structure of the dimer.
Task 25. Isomerism of Octahedral Fe Complexes

Fe(N,N')$_2$Cl$_2$ has an octahedral structure featuring two bidentate, neutral α-iminopyridine (N,N') ligands, whose structure is shown below.

\[
\begin{align*}
\text{\(N\)} & \quad \text{\(\text{\(N\)}\)} \\
\text{\(N\)} & \quad \text{\(N\)} \\
\text{\(\text{\(N\)}\)} & \quad \text{\(\text{\(N\)}\)} \\
\text{\(N\)} & \quad \text{\(N\)} \\
\text{\(N\)} & \quad \text{\(N\)} \\
\text{\(N\)} & \quad \text{\(N\)}
\end{align*}
\]

25.1) Draw all possible isomers of Fe(N,N')$_2$Cl$_2$.

25.2) Which isomers of Fe(N,N')$_2$Cl$_2$ are optically active?

Task 26. Stoichiometry and Structure Determination

Compound A consists only of three elements C, H, and O. Under standard conditions, A is a yellow solid with molar mass of 166.2 g mol$^{-1}$. By weight, A has 28.9% O and 65.0% C.

26.1) Determine chemical formula of A.

26.2) A contains a phenol functional group with intramolecular hydrogen bonding. The $^1$H and $^{13}$C($^1$H) NMR spectra of A in CDCl$_3$ are shown below. Based on your answer in 26.1, draw a chemical structure of A, and show the intramolecular hydrogen bond(s).

*NMR data were obtained from Sigma-aldrich.com.
26.3) From the reaction scheme below, draw chemical structures of \( X \), \( Y \), and \( Z \).

\[
2 \quad A + H_2N\text{NH}_2 \quad \xrightarrow{-2 \ Y} \quad X \quad \xrightarrow{\text{Cu(OOCCH}_3)_2} \quad Z
\]

**Task 27. Atropine**

Atropine is an organic compound used to treat certain types of nerve agent and pesticide poisonings. This compound can be synthesized from tropine and tropic acid in one step.

27.1) Tropine can be prepared as shown in the diagram below. The first step of this synthesis is “double Mannich reaction” (Robinson, 1917).

Write down the structural formulae of compounds \( A \) and \( B \).

27.2) Tropic acid can be prepared from the reaction of acetophenone and HCN followed by hydrolysis, elimination, addition and nucleophilic substitution (Mackenzie and Ward, 1919). In this synthesis, it should be noted that the electrophilic addition by HCl did not follow Markovnikov's Rule, and the anti-Markovnikov product (\( E \)) was obtained.

Tropic acid (\( F \)) can also be prepared in only three steps from ethyl 2-bromo-2-phenylacetate and paraformaldehyde (Pernot, 1950). NMR data of tropic acid (\( F \)) are provided below.

\(^1\text{H NMR (400 MHz, CDCl}_3) \delta 3.76-3.83 (2H, m), 4.80 (1H, dd, } J = 8.1 \text{ Hz), 7.21-7.30 (5H, m) and 2 broad peaks at } \sim 5 \text{ ppm and } \sim 12 \text{ ppm.}

\(^{13}\text{C NMR (100 MHz, CD}_3\text{OD) } \delta 55.9, 65.1, 128.5, 129.2, 129.7, 137.9, 176.1

Write down the structural formulae of compounds \( C-G \) in the diagram below.
27.3) When tropine was combined with tropic acid under acidic conditions, atropine was produced. Write down the structural formula of atropine.

\[
\text{B (tropine, C}_{8}\text{H}_{15}\text{NO)} + \text{F (tropic acid, C}_{9}\text{H}_{10}\text{O}_{3}) \xrightarrow{H^+} \text{H (atropine, C}_{17}\text{H}_{23}\text{NO}_{3})
\]

27.4) Predict the major products of the reactions shown below. $^{13}$C NMR spectrum of compound I shows nine signals in the range of 0-80 ppm, four signals in the range of 120-140 ppm, and one signal at 155 ppm. $^{13}$C NMR spectrum of compound J shows eight signals in the range of 0-80 ppm and one signal at 155 ppm. $^{13}$C NMR spectrum of compound K shows seven signals in the range of 0-80 ppm and four signals in the range of 120-140 ppm.
Task 28. Synthesis of Building Blocks for Fluorescent Markers

Carboxy-functionalized fluorescein dyes, which have been employed as important conjugated fluorescent markers of biologically active compounds, can be synthesized based on the improved synthetic route developed by M.H. Lyttle and co-workers (Lyttle, M. H.; Carter, T. G.; and Cook, R. M. *Org. Proc. Res. Dev.* 2001, 5, 45–49). In these synthetic sequences, two different precursors (C and I) were required and they were synthesized as followed.

Identify compounds A–I.
**Task 29. Synthesis towards Anatoxin-a**

Anatoxin-a (I) is a secondary amine alkaloid with acute neurotoxicity that can cause death by respiratory paralysis. This compound is produced by several different genera of cyanobacteria found all over the world. In 2004, Jehrod B. Brenneman and Stephen F. Martin reported a concise synthesis of anatoxin-a from commercially available $\delta$-methyl pyroglutamate, which was converted to compound A. Write down the structural formulae of compounds B, C, F, H and I in the boxes provided.

![Diagram of the synthesis process involving compounds A to I.](image-url)
**Task 30. Total Synthesis of Illudin C**

During the synthesis of sesquiterpene (±)-illudin C, R. L. Funk required the building block C which could be prepared based on the short synthesis shown below (Aungst, Jr., R. A.; Chan, C.; Funk, R. L. *Org. Lett.* 2001, 3, 2611–2613.) Compound C was then carried on in the synthesis as shown. Provide the correct structures of A, B, C and D.

![Synthesis Scheme](image)

**Task 31. Total Synthesis of μ-Opioid Receptor (MOR) Agonists**

In the studies of pain management, μ-opioid receptor has been an important protein target in the central nervous system which interacts with specific small molecules and may therefore alleviate pain in patients. In studying this target, one needs to have access to these compounds. Nature has been a major source of these small compounds which may be used in the research. In addition to the parent compounds in plants which are known to reduce pain, synthetic derivatives are also equally important for the study. In a recent pharmacological evaluation of the synthetic mitragynine and derivatives, the principle alkaloids found in the Southeast Asian plant *Mitragyna speciosa* (known as Kratom in Thailand), by Sames and co-workers (Kruegel, A. C.; Gassaway, M. M.; Kapoor, A.; Váradi, A.; Majumdar, S. Filizola, M.; Javitch, J. A.; and Sames, D. *J. Am. Chem. Soc.* 2016, 138, 6754–6764), the materials for the evaluation were accessed via total synthesis. The brief synthesis is illustrated in the scheme below.
31.1) Draw the correct structure of compound A.

31.2) Identify the structures of compounds B-D with correct stereochemistry.
Task 32. Pericyclic Reaction

32.1) A series of pericyclic reaction can be used to construct complex organic molecular structure in a stereocontrolled manner. For example, Moore, et al. (J. Org. Chem. 1998, 63, 6905.) reported the synthesis of triquinane derivatives from the corresponding cyclobutenone as shown in scheme below.

Propose structures of intermediates A and B.

32.2) In the synthesis of prostaglandin, Corey, et al. (J. Am. Chem. Soc. 1969, 91, 5675.) used cycloaddition reaction as a key step along with a series of straightforward chemical transformations to set up stereochemistry at the periphery of cyclopentyl structure as shown in scheme below.
(i) Identify structures of compounds C-G with correct relative stereochemistry.

(ii) There is a carbon, labeled with an asterisk in compound 3. Indicate the position of this labeled carbon in either compound 1 or 2 by placing an asterisk on the carbon in the given structure.

(iii) If a student synthesizes compound 3 from compounds 1 and 2 by following the synthetic scheme above, how many possible stereoisomers of compound 3 can the student obtain?
32.3) 1,3-Dipolar cycloaddition is a powerful tool for the construction of heterocyclic structure. For example, upon heating, compound H undergoes intramolecular [4+2]-cycloaddition to yield compound I. Reduction of a weak N-O bond of compound I by catalytic hydrogenation gave product J.

\[
\begin{align*}
&\text{O}^- \quad \text{N}^+ \\
\text{H} \quad \text{I} \quad \text{J} \\
&\text{C}_7\text{H}_{11}\text{NO} \quad \text{H}_2\text{Pd-C}
\end{align*}
\]

(i) Propose structures of compounds I and J.

(ii) If a racemic mixture of H is used in the reaction, write all possible stereoisomer(s) of products J.

**Task 33. Stereoisomers without Stereocenter**

Axial chirality refers to stereoisomerism of a special case of chirality in which a molecule does not possess a stereogenic center but an axis of chirality. An axis of chirality is defined as an axis about which a set of substituents is held in a spatial arrangement that is not superimposable on its mirror image.

Two necessary preconditions for axial chirality are:
- A rotationally stable axis
- Presence of different substituents on both sides of the axis

Axial chirality is most commonly observed in atropisomeric biaryl compounds wherein the rotation about the aryl-aryl bond is restricted, for example, biphenyl, binaphthyls. Certain allene compounds also display axial chirality.

33.1) From the given structures, draw 3-D structure and the corresponding mirror image of the given compounds. Use plane of symmetry to determine whether they are chiral or achiral.

(i)

\[
\begin{align*}
\text{H} & \quad \text{C} & \quad \text{CH}_3 \\
\text{H} & \quad \text{Cl} & \quad \text{Cl}
\end{align*}
\]

(ii)

\[
\begin{align*}
\text{Cl} & \quad \text{C} & \quad \text{H} \\
\text{H} & \quad \text{Cl} & \quad \text{Cl}
\end{align*}
\]
33.2) Enantiomers of medium ring trans-cycloalkenes exist. For example, trans-cyclooctene can be resolved and its enantiomers are stable at room temperature. On the other hand, trans-cyclononene has also been resolved but it racemizes with a half-life of 4 min. at 0°C.

(i) Draw mirror images of the given structures of trans-cyclooctene and trans-cyclononene.

(ii) Why does trans-cyclononene racemize faster than trans-cyclooctene?
Part 2. Practical Tasks

The safety rules and regulations

Regulations of the International Chemistry Olympiad (IChO)

Safety

1. During the experimental part, the competitors must wear laboratory coats and eye protection. The competitors are expected to bring their own laboratory coats. Other means of protection for laboratory work are provided by the organizer.

2. When handling liquids, each student must be provided with a pipette ball or filler. Pipetting by mouth is strictly forbidden.

3. The use of acutely toxic substances (GHS hazard statement H300, H310, H330) is strictly forbidden. The use of toxic substances is not recommended, but may be allowed if special precautions are taken. Substances with GHS hazard statements H340, H350, H360 (proven mutagens, carcinogens, and teratogens) must not be used under any circumstances (see Appendix B for definitions of these categories).

4. Detailed recommendations involving students’ safety and the handling and disposal of chemicals can be found in Appendices A 1, A 2, and B.
   
   Appendix A 1: Safety Rules for Students in the laboratory.
   
   Appendix A 2: Safety Rules and Recommendations for the Host Country of the IChO.
   
   Appendix B contains a reference to the hazard symbols and statements of the Globally Harmonized System of Classification of Chemicals (GHS), the use of which is expected in labeling and classifying materials used at the IChO.
**Task P1. Quantitative Determination of Ascorbic Acid and Citric Acid in Beverages**

The weather in Thailand is generally hot and humid which may cause discomfort and fatigue. Therefore drinking of water or beverage is optional choice to refresh and reduce an appetite. There are various brands of drink available in the markets. The main components in the beverage are sweetener, organic acid, minerals as well as color and flavor. These components basically improve the taste and texture.

In this task, you will determine the amount of ascorbic acid (C$_6$H$_8$O$_6$) and citric acid (C$_3$H$_5$O$_3$(COOH)$_3$) that are in a beverage sample by two titrations.

A) Determination of ascorbic acid by redox titration

B) Determination of total acid content by acid-base titration


**Chemicals**

- 0.001 mol dm$^{-3}$ KI$_O_3$
- 1 mol dm$^{-3}$ HCl
- 0.5% w/v starch solution
- 0.1 mol dm$^{-3}$ NaOH*
- 0.5% w/w phenolphthalein indicator
- KI
- Sample (containing 1.28x10$^{-3}$ mol dm$^{-3}$ ascorbic acid and 6.76x10$^{-2}$ mol dm$^{-3}$ citric acid)

**Glasswares**

- 2 burets
- 50 cm$^3$ -volumetric pipet
- 10 cm$^3$ -volumetric pipet
- pipet bulb
- 6 Erlenmeyer flasks

* This solution must be standardized. Use potassium hydrogen phthalate, KHP for the standardization.
A) Determination of ascorbic acid by redox titration

1. Fill a buret with 0.001 mol dm\(^{-3}\) KIO\(_3\).

2. Pipet a 50.00 cm\(^3\) aliquot of sample solution and quantitatively transfer it to an Erlenmeyer flask. Add 1 gram of KI, 5 cm\(^3\) of 1 M HCl and 3 cm\(^3\) of 0.5 % starch solution to the flask.

3. Titrate with 0.001 mol dm\(^{-3}\) KIO\(_3\) immediately.

4. Endpoint is marked by the appearance of the blue starch–I\(_3^-\) complex.

5. Repeat with two additional 50.00 cm\(^3\) aliquots.

The amount of ascorbic acid is determined by titration with KIO\(_3\). The reaction equations are shown as equations (1) – (4).

\[
\begin{align*}
\text{IO}_3^- + 5\text{I}^- + 6\text{H}^+ & \rightarrow 3\text{I}_2 + 3\text{H}_2\text{O} \quad (1) \\
\text{C}_6\text{H}_8\text{O}_6 + \text{I}_2 & \rightarrow \text{C}_6\text{H}_6\text{O}_6 + 2\text{H}^+ + 2\text{I}^- \quad (2) \\
\text{I}_2 + \text{I}^- & \rightarrow \text{I}_3^- \quad (3) \\
\text{I}_3^- + \text{starch} & \rightarrow \text{starch} - \text{I}_3^- \text{ complex} \quad (4) 
\end{align*}
\]

(i) Fill the data in the Table.

<table>
<thead>
<tr>
<th>Titration no.</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial reading of the burette, cm(^3)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Final reading of the burette, cm(^3)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Consumed KIO(_3) volume, cm(^3)</td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

(ii) Calculate mg of ascorbic acid per 100 cm\(^3\) of sample.
B) Determination of total acid content by acid-base titration

1. Pipet a 10.00 cm$^3$ aliquot of the sample solution and quantitatively transfer it to Erlenmeyer flask.

2. Add 2-3 drops of phenolphthalein indicator to the flask.

3. Slowly add NaOH from the buret to the flask.

4. At the endpoint, color of the indicator will change from colorless to pink.

5. Repeat with two additional 10.00 cm$^3$ aliquots.

Titration with NaOH therefore determines the amount of total acid in the sample. The reaction equations are shown as equations (5) – (6).

\[
\text{C}_6\text{H}_8\text{O}_6 + \text{NaOH} \rightarrow \text{C}_6\text{H}_7\text{O}_6\text{Na} + \text{H}_2\text{O} \quad (5)
\]
\[
\text{C}_3\text{H}_5\text{O(COOH)}_3 + 3\text{NaOH} \rightarrow \text{C}_3\text{H}_5\text{O(COO)}_3\text{Na}_3 + 3\text{H}_2\text{O} \quad (6)
\]

(i) Fill the below Table

<table>
<thead>
<tr>
<th>Titration no.</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial reading of the buret, cm$^3$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Final reading of the buret, cm$^3$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Consumed base volume, cm$^3$</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(ii) Calculate number of moles of reacted hydroxide

The amount of citric acid determined by difference as shown below.

moles NaOH neutralized (total acid) - moles NaOH neutralized (ascorbic acid) 

\[= \text{moles NaOH neutralized (citric acid)}\]

(iii) Calculate grams of citric acid per 100 cm$^3$ of sample
**Task P2. Spectrophotometric Determination of Chromium and Manganese**

According to Beer’s law, the net absorbance is an additive of each solute, provided there is no reaction between the two solutes.

\[
A_{\text{total} \lambda 1} = A_{X \lambda 1} + A_{Y \lambda 1}
\]

\[
A_{\text{total} \lambda 2} = A_{X \lambda 2} + A_{Y \lambda 2}
\]

where \( A_{\text{total} \lambda 1} \) and \( A_{\text{total} \lambda 2} \) are the net measured absorbances at \( \lambda 1 \) and \( \lambda 2 \) respectively, and \( A_X \) and \( A_Y \) are the absorbances of the two solutes.

**Chemicals**

- 0.5 mol dm\(^{-3}\) H\(_2\)SO\(_4\)
- 0.01 mol dm\(^{-3}\) KMnO\(_4\)
- 0.01 mol dm\(^{-3}\) K\(_2\)Cr\(_2\)O\(_7\)

**Instrument**

Visible Spectrophotometer

**Glasswares**

- 2.00 cm\(^3\) measuring pipet (2)
- 10.00 cm\(^3\) measuring pipet (2)
- 50.00 cm\(^3\) volumetric flask (13)
- pipet bulb

**A) Determination of molar absorption coefficients of KMnO\(_4\) and K\(_2\)Cr\(_2\)O\(_7\)**

1. Prepare standard KMnO\(_4\) solutions of 0.5 x \(10^{-4}\), 1.0 x \(10^{-4}\), 2.0 x \(10^{-4}\), 5.0 x \(10^{-4}\) mol dm\(^{-3}\) in 0.5 mol dm\(^{-3}\) H\(_2\)SO\(_4\) by appropriate dilution from standard 0.01 mol dm\(^{-3}\) KMnO\(_4\) solution to the final volume of 50.00 cm\(^3\) in volumetric flask.

2. Prepare standard K\(_2\)Cr\(_2\)O\(_7\) solutions of 2.0 x \(10^{-4}\), 3.0 x \(10^{-4}\), 4.0 x \(10^{-4}\), 6.0 x \(10^{-4}\) mol dm\(^{-3}\) in 0.5 mol dm\(^{-3}\) H\(_2\)SO\(_4\) by appropriate dilution from standard 0.01 mol dm\(^{-3}\) K\(_2\)Cr\(_2\)O\(_7\) solution to the final volume of 50.00 cm\(^3\) in volumetric flask.
3. Record the absorbance values of all solutions at 440 and 545 nm

<table>
<thead>
<tr>
<th>KMnO₄ (mol dm⁻³)</th>
<th>Absorbance (A) (at 440 nm)</th>
<th>Absorbance (A) (at 545 nm)</th>
<th>Molar absorption coefficient (at 440 nm)</th>
<th>Molar absorption coefficient (at 545 nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5 x 10⁻⁴</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.0 x 10⁻⁴</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.0 x 10⁻⁴</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.0 x 10⁻⁴</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Molar absorption coefficient (average)

<table>
<thead>
<tr>
<th>K₂Cr₂O₇ (mol dm⁻³)</th>
<th>Absorbance (A) (at 440 nm)</th>
<th>Absorbance (A) (at 545 nm)</th>
<th>Molar absorption coefficient (at 440 nm)</th>
<th>Molar absorption coefficient (at 545 nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.0 x 10⁻⁴</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.0 x 10⁻⁴</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.0 x 10⁻⁴</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6.0 x 10⁻⁴</td>
<td></td>
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</tr>
</tbody>
</table>

Molar absorption coefficient (average)

B) Determination the concentrations of KMnO₄ and K₂Cr₂O₇ in solution mixture

1. Prepare a solution containing 5.0 cm³ of KMnO₄ 0.5 x 10⁻⁴ mol dm⁻³ and 5.0 cm³ of K₂Cr₂O₇ 6.0 x 10⁻⁴ mol dm⁻³ (Solution A)

2. Prepare a solution containing 5.0 cm³ of KMnO₄ 2.5 x 10⁻⁴ mol dm⁻³ and 5.0 cm³ of K₂Cr₂O₇ 4.0 x 10⁻⁴ mol dm⁻³ (Solution B)

3. Prepare a solution containing 5.0 cm³ of KMnO₄ 5.0 x 10⁻⁴ mol dm⁻³ and 5.0 cm³ of K₂Cr₂O₇ 2.0 x 10⁻⁴ mol dm⁻³ (Solution C)

4. Record the absorbance values of all solutions at 440 and 545 nm

<table>
<thead>
<tr>
<th>Solution</th>
<th>Absorbance (A) (at 440 nm)</th>
<th>Absorbance (A) (at 545 nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Calculate the concentration of KMnO₄ and K₂Cr₂O₇ in each solution (from the experimental absorbance values)

<table>
<thead>
<tr>
<th>Solution</th>
<th>KMnO₄ (mol dm⁻³)</th>
<th>% error</th>
<th>K₂Cr₂O₇ (mol dm⁻³)</th>
<th>% error</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B</td>
<td></td>
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</tr>
<tr>
<td>C</td>
<td></td>
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</tbody>
</table>
Task P3. Synthesis of “Ferrocenated” Iron Oxide Nanoparticles and Their Activities in the Decolorization of Methylene Blue

Ferrocenated compounds are a mixture containing ferrocene, iron oxide, and cyclopentadienyl radical. The preparation of ferrocenated compounds can be done by the decomposition of ferrocenium in basic condition. Cyclopentadienyl radical in ferrocenated compounds is an active specie to generate reactive oxygen species for the decolorization of methylene blue.

In this task, you will:

- Perform the synthesis of ferrocenated iron oxide nanoparticles by coprecipitation.
- Perform the decolorization of methylene blue by ferrocenated iron oxide, and follow reaction by spectrophotometric analysis.

**Chemicals**

- Ferric chloride hexahydrate (FeCl₃·6H₂O)
- Ferrous chloride tetrahydrate (FeCl₂·4H₂O)
- Ferrocene
- Concentrated sulfuric acid
- De-ionized water
- Sodium hydroxide
- Barium chloride
- Methylene blue

**Glasswares**

- Round-bottomed flask, 250 cm³
- Beaker, 100 cm³
- Erlenmeyer flask, 250 cm³
- Graduated cylinder, 10 cm³
- Test tubes
- Magnetic bars
- Evaporation dish
- Aluminum foil
- Beaker, 25 cm³
- Beaker, 250 cm³
- Volumetric flask, 250 cm³
- Graduated cylinder, 100 cm³
- Pasteur pipets and rubber bulb
- Stirring rods
- Centrifuge tubes

**Instruments**

- Stirrer
- pH meter
- Oven
- 4-digit balance
- Centrifuge
- Visible Spectrophotometer
Synthesis of ferrocenated iron oxide nanoparticles

1. Add concentrated sulfuric acid (0.5 cm$^3$) to ferrocene (6.84 g) to yield a ferrocenium solution. Do this experiment in a fume hood.
2. Add the ferrocenium solution to water (5 cm$^3$) and stir for 30 minutes.
3. Prepare a mixed solution of ferrous chloride tetrahydrate (1.55 g) and ferric chloride hexahydrate (4.15 g) in de-ionized water (80 cm$^3$).
4. Add the mixed solution into the blue solution of ferrocenium and then stir for 1 hour.
5. Add a saturated NaOH solution slowly until the pH of solution is 12.
6. Collect the orange precipitate by centrifugation at 4500 rpm for 20 minutes.
7. Wash the precipitate with de-ionized water. Be sure that sulfate ion is completely washed by checking with BaCl$_2$ solution.
8. Dry orange solid at 100 °C for 1 hour. Record the weight and calculate the yield of the ferrocenated iron oxide.

Decolorization of methylene blue

1. Prepare a solution of methylene blue (9.97×10$^{-6}$ mol dm$^{-3}$).
2. Add 100 cm$^3$ of methylene blue in a 250 cm$^3$-Erlenmeyer flask which is wrapped with aluminum foil. Keep this flask in a dark box while stirring.
3. Add the prepared orange solid (0.100 g) into the solution of methylene blue.
4. Collect 3 cm$^3$ of the mixture at every 5 minutes.
5. Centrifuge the mixture at 4500 rpm for 3 minutes.
6. Take the clear supernatant for spectrophotometric analysis.
7. Plot a graph between the absorbance at a specific wavelength and reaction time.

You may prepare iron oxide by repeating the above experiments without the addition ferrocene and perform the decolorization of methylene blue for comparison with ferrocenated iron oxide.
**Task P4. Synthesis of Aspirin**

Aspirin or acetylsalicylic acid (ASA) is a well-known medication for the treatment of pain, fever, and inflammation. It is a nonsteroidal anti-inflammatory drug (NSAID). Aspirin irreversibly inhibits COX enzyme results in the decrease in the production of prostaglandins and thromboxanes, the key molecules that affect various physiological responses including transmission of pain, regulation of inflammation and fever, as well as aggregation of platelets.

In this task, you will:

- Perform the synthesis of acetylsalicylic acid via the esterification of salicylic acid with acetic anhydride.
- Calculate % yield of the purified product.
- Perform thin layer chromatography analysis.

**Chemicals**

- Acetic anhydride
- Ethyl acetate
- Concentrated H$_2$SO$_4$ (18 mol dm$^{-3}$)
- Hexane
- Distilled Water
- Ice (for an ice bath)
- Ethanol
- Salicylic acid

**Glasswares**

- Beaker, 100 cm$^3$
- Buchner funnel
- Crystallizing dish (for a hot water bath and an ice bath)
- Erlenmeyer flasks, 125 cm$^3$ and 250 cm$^3$
- Filter paper
- Graduated cylinder, 25 cm$^3$
- Pasteur pipet and rubber bulb
- Stirring rod
- Spatula
- Suction flask
- Capillary tube for TLC
- TLC plate on aluminum foil or glass supports and TLC jar

**Instruments**

- Analytical balance (± 0.0001 g)
- Hotplate
- Water aspirator or vacuum pump
- Stand and clamps
**Procedure:**

1. Weigh out 5.00 g of salicylic acid. Transfer this to a 125 cm$^3$ Erlenmeyer flask. Record the mass.

2. In the hood, add 7.0 cm$^3$ of acetic anhydride to the flask contained salicylic acid.

3. Carefully add 8 drops of concentrated sulfuric acid (18 mol dm$^{-3}$) to the reaction flask.

4. Assemble a hot water bath using a beaker and a hotplate.

5. Place the flask in the water bath and heat. After the water begins to boil, heat for an additional 15 minutes.

6. Allow the reaction flask to cool down for few minutes.

7. Carefully add 15.0 cm$^3$ of room temperature water to the flask. Swirl the flask to mix the contents.

8. Place the reaction flask in an ice bath. Let it cool down until the crystallization of the product completes (approx. 15 minutes). If crystals do not appear, scratch the walls of the flask with a stirring rod to induce crystallization.

9. Collect the solid product by vacuum filtration using a Buchner funnel.

10. Transfer the solid product from the Buchner funnel to a 250 cm$^3$ Erlenmeyer flask. Recrystallize the crude product with ethanol and water.

**Recrystallization Protocol:** Add preheated ethanol until the product is all dissolved. While heating the solution, add water dropwise and swirl. Keep adding water until the solution becomes cloudy. To the cloudy solution, hot ethanol is added dropwise until the solution becomes clear. Remove the flask from heating and allow the solution to cool down undisturbed to the room temperature. Crystals should form. Chill the flask containing crystals in an ice-water bath to complete crystallization.

11. Collect the crystalline product using by vacuum filtration using a Buchner funnel.

12. Dry the product. Record weight and determine % yield

13. Perform thin layer chromatography (TLC) to determine the purity of the purified product.
Task P5. Synthesis of Benzopinacolone

The pinacol–pinacolone rearrangement can be used to convert 1,2-diol to carbonyl compound. The reaction takes place under acidic conditions. In this experiment, benzopinacol could be transformed to benzopinacolone via acid-catalyzed carbocation rearrangement.

In this task, you will:

Perform the acid catalyzed pinacol–pinacolone rearrangement.
Calculate % yield of the purified product.

Chemicals

Benzopinacol
Ethyl acetate
Glacial acetic acid
Hexane
Iodine
Ice (for an ice bath)
Silicone oil or alike for oil bath

Glasswares

Beaker, 600 cm$^3$
Buchner funnel
Erlenmeyer flask, 125 cm$^3$
Filter paper
Ice bath
Graduated cylinder, 25 cm$^3$
Magnetic bar or boiling chip

Instruments

Analytical balance (± 0.0001 g)
Hotplate stirrer
Water aspirator or vacuum pump
Stand and clamps
**Procedure:**

1. Place 25 cm$^3$ of glacial acetic acid and 0.1 g of iodine in a 100 cm$^3$ round-bottomed flask equipped with a reflux condenser.

2. Add 0.015 mol of benzopinacol. (Benzopinacol could be prepared from photochemical reaction of benzophenone and isopropyl alcohol, see appendix C.)

3. Reflux the solution for 10 minutes in a hot oil bath.

4. Cool the reaction mixture to room temperature.

5. Collect the solid by vacuum filtration using Buchner funnel. Record the mass of crude product.

6. Recrystallize the crude product with the mixture of ethyl acetate and hexane (*The recrystallization protocol is similar to that described in Task P4*).

7. Collect the crystals by vacuum filtration using Buchner funnel. Record the mass of recrystallized product.

8. Determine the yield of the product.
APPENDICES

APPENDIX A

A1: SAFETY RULES FOR STUDENTS IN THE LABORATORY

All students of chemistry must recognize that hazardous materials cannot be completely avoided. Chemists must learn to handle all materials in an appropriate fashion. While it is not expected that all students participating in the International Chemistry Olympiad know the hazards of every chemical, the organizers of the competition will assume that all participating students know the basic safety procedures. For example, the organizers will assume that students know that eating, drinking or smoking in the laboratory or tasting a chemical is strictly forbidden.

In addition to the common-sense safety considerations to which students should have been previously exposed, some specific rules, listed below, must also be followed during the Olympiad. If any question arises concerning safety procedures during the practical exam, the student should not hesitate to ask the nearest supervisor for direction.

Rules regarding personal protection

1. Eye protection must be worn in the laboratories at all times. If the student wears contact lenses, full protection goggles must also be worn. Eye protection will be provided by the host country.
2. A laboratory coat is required. Each student will supply this item for himself/herself.
3. Long pants and closed-toed shoes are recommended for individual safety. Long hair and loose clothing should be confined.
4. Pipetting by mouth is strictly forbidden. Each student must be provided with pipette bulb or pipette filler.

Rules for Handling Materials

1. Specific instructions for handling hazardous materials will be included by the host country in the procedures of the practical exam. All potentially dangerous materials will be labeled using the GHS symbols. Each student is responsible for recognizing these symbols and knowing their meaning (see Appendix B).
2. Do not indiscriminately dispose chemicals in the sink. Follow all disposal rules provided by the host country.

A2: SAFETY RULES AND RECOMMENDATIONS FOR THE HOST COUNTRY OF THE INTERNATIONAL CHEMISTRY OLYMPIAD

Certainly it can be assumed that all students participating in the IChO have at least modest experience with safety laboratory procedures. However, it is the responsibility of the International Jury and the organizing country to be sure that the welfare of the students is carefully considered.
Reference to the Safety Rules for Students in the Laboratory will show that the students carry some of the burden for their own safety. Other safety matters will vary from year to year, depending on practical tasks. The organizers of these tasks for the host country are therefore assigned responsibility in the areas listed below. The organizers are advised to carefully test the practical tasks in advance to ensure the safety of the experiments. This can best be accomplished by having students of ability similar to that of IChO participants carry out the testing.

APPENDIX B

HAZARD WARNING SYMBOLS AND HAZARD DESIGNATIONS

Chemicals used in the IChO laboratory experiments need to be labeled according to the Globally Harmonized System of Labelling of Chemicals (GHS) standard developed by the United Nations. The organizing country should use the locally legislated GHS system (pictograms, hazard statements, etc.) if it exists. If such rules do not exist, the original GHS directives (http://www.unece.org/trans/danger/publi/ghs/ghs_welcome_e.html) and the GHS compliant documentation by the chemical providers should be used.
APPENDIX C

Synthesis of benzopinacol
Org. Synth. 1934, 14, 8.
DOI: 10.15227/orgsyn.014.0008

![Chemical structure](image)

**Procedure**

A mixture of 150 g (0.82 mol) of benzophenone, 1 drop of glacial acetic acid, and 665 g (850 cm³, 11 mol) of isopropyl alcohol in a 1L round-bottomed flask is warmed to 45 °C. The flask is closed with a tight cork firmly wired or tied in place, and is supported in an inverted position in a tripod and exposed to direct sunlight. After 3-5 hours under the sunlight, crystals of benzopinacol should be observed; after 8-10 days of exposure to the sunlight (See **Note**), the crystals of benzopinacol should be completely formed. Chill the reaction flask containing crystals in the ice bath to complete crystallization. The crystalline product is collected by vacuum filtration, filtered using Buchner funnel. The crystalline product is washed with a small quantity of isopropyl alcohol, and allowed to air dry. The product should be sufficiently pure for most purposes. It may be crystallized by dissolving it in hot benzene, filtering, and adding 400 cm³ of hot ligroin (b.p. 90–100 °C) to the hot filtrate. After cooling in ice and filtering there is obtained 129–130 g of purified product.

**Note:**

About 5 days of bright sunlight exposure are required to complete the reduction. The reaction can be interrupted at any time, the crystals filtered, and the filtrate then exposed further.