

# ICHO 2026

理论题与解答 · 乌兹别克斯坦塔什干 · 9 道理论题及完整解答

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## 题目 1：穿越时空之旅：阿维森纳的秘密

### T1. 穿越时空之旅：阿维森纳的秘密

7%

| 1.1 | 1.2 | 1.3 | 1.4 | 1.5 | 1.6 | Σ  |
|-----|-----|-----|-----|-----|-----|----|
| 3   | 4   | 3   | 4   | 7   | 4   | 25 |

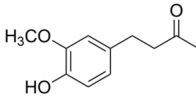
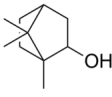
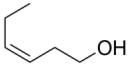
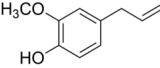
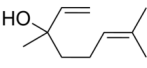
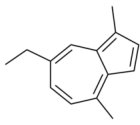
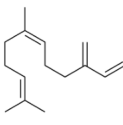
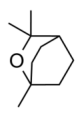


一位化学家发现自己来到了 11 世纪，并在那里遇见了著名医师阿维森纳。在阿维森纳的实验室里，她发现了一种蓝色药剂和一块黄色的神秘石头。她将它们带回了 2026 年。为了揭开它们的组成之谜，她开始了研究。

#### 第 1 部分. 蓝色药剂

首先，这位化学家编制了一张表，列出了她在阿维森纳的实验室里见到的、仅有的四种可能用于配制该药剂的植物名称，以及可从这些植物中提取的化合物。

| 植物   | 可提取的化合物                                             |                                                     |                                       |
|------|-----------------------------------------------------|-----------------------------------------------------|---------------------------------------|
| 姜属   | 1 (C <sub>11</sub> H <sub>14</sub> O <sub>3</sub> ) | 2 (C <sub>10</sub> H <sub>18</sub> O)               | 3 (C <sub>10</sub> H <sub>18</sub> O) |
| 金丝桃属 | 4 (C <sub>6</sub> H <sub>12</sub> O)                | 5 (C <sub>10</sub> H <sub>12</sub> O <sub>2</sub> ) | 6 (C <sub>10</sub> H <sub>18</sub> O) |
| 母菊属  | 7 (C <sub>14</sub> H <sub>16</sub> )                | 8 (C <sub>15</sub> H <sub>24</sub> )                | 3 (C <sub>10</sub> H <sub>18</sub> O) |
| 蒿属   | 9 (C <sub>10</sub> H <sub>16</sub> O)               | 10 (C <sub>10</sub> H <sub>18</sub> O)              | 3 (C <sub>10</sub> H <sub>18</sub> O) |

| Plants            | Compounds that can be extracted                                                     |                                                                                     |                                                                                       |
|-------------------|-------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------|
| <i>Zingiber</i>   |  |  |  |
|                   | 1 (C <sub>11</sub> H <sub>14</sub> O <sub>3</sub> )                                 | 2 (C <sub>10</sub> H <sub>18</sub> O)                                               | 3 (C <sub>10</sub> H <sub>18</sub> O)                                                 |
| <i>Hypericum</i>  |  |  |  |
|                   | 4 (C <sub>6</sub> H <sub>12</sub> O)                                                | 5 (C <sub>10</sub> H <sub>12</sub> O <sub>2</sub> )                                 | 6 (C <sub>10</sub> H <sub>18</sub> O)                                                 |
| <i>Chamomilla</i> |  |  |  |
|                   | 7 (C <sub>14</sub> H <sub>16</sub> )                                                | 8 (C <sub>15</sub> H <sub>24</sub> )                                                | 3 (C <sub>10</sub> H <sub>18</sub> O)                                                 |

|           |                                                                                   |                                                                                   |                                                                                     |
|-----------|-----------------------------------------------------------------------------------|-----------------------------------------------------------------------------------|-------------------------------------------------------------------------------------|
| Artemisia |  |  |  |
|           | 9 (C <sub>10</sub> H <sub>16</sub> O)                                             | 10 (C <sub>10</sub> H <sub>18</sub> O)                                            | 3 (C <sub>10</sub> H <sub>18</sub> O)                                               |

通过色谱分析，她确定该药剂由四种不同的物质（X、Y、Z 和 W）组成。

随后，这位化学家发现，X 在酸性介质中可异构化为 Y，且 Y 具有一个对称面。

#### 1.1 确定 X 和 Y。— 3.0 分

色谱分析还表明，使药剂呈蓝色的是物质 Z。Z 是一种熟知的物质 A 的衍生物，A 具有两个相互垂直的对称面。加热时，A 异构化为芳香族化合物 B，后者具有三个两两垂直的对称面。对物质 Z 进行氯化后，在质谱中分别于  $m/z$  218 和 220 处观察到一对强度比为 3:1 的峰。

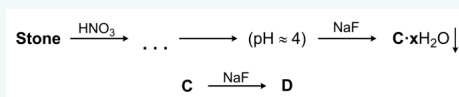
#### 1.2 确定 Z，并画出物质 A 和 B 的结构。— 4.0 分

这位化学家从药剂中提取出了 W。将 W 加入  $\text{Fe}^{3+}$  水溶液时，观察到了特征性的颜色变化。对 W 的质谱分析显示，峰强度比为  $[\text{M}]^+ : [\text{M} + 1]^+ = 9 : 1$ ，其中 M 为分子离子。假设碳仅由  $^{12}\text{C}$  和  $^{13}\text{C}$  组成， $^{12}\text{C}$  的天然同位素丰度为 98.9%，其他所有元素均为单一同位素。

#### 1.3 根据质谱数据确定碳原子数 ( $n$ )，并确定 W。写出计算过程。— 3.0 分

#### 第 2 部分. 神秘的石头

阿维森纳曾告诉她，这块石头是一种化学计量化合物。她将其溶于稀硝酸中。随后，她将溶液的 pH 调节至约 4，并加入 NaF。这使溶液中生成了沉淀  $\text{C} \cdot x\text{H}_2\text{O}$ ，其中水的质量分数为 39.16%。无水 C 与过量 NaF 反应生成化合物 D，其中钠和金属 Q 的质量分数分别为 32.85% 和 12.85%，且 D 用于 Q 的工业生产。



#### 1.4 确定金属 Q 以及化合物 $\text{C} \cdot x\text{H}_2\text{O}$ 和 D。— 4.0 分

阿维森纳告诉她，他是在一处煤矿床中发现这块石头的。这块石头含有一种高度对称的酸 F 的阴离子。F 与  $\text{P}_2\text{O}_5$  反应生成二元化合物 G，其中氧的质量分数为 49.98%，且具有一条三重对称轴。用高锰酸钾在酸性溶液中氧化化合物 E，可以制得 F。E 中氢的质量分数为 11.18%，且具有一条六重对称轴。



#### 1.5 画出 E、F 和 G 的结构。— 7.0 分

接着，她在空气中对这块石头进行了热重分析。一份 10.00 g 的样品在约  $100^\circ\text{C}$  时开始失重，到  $200^\circ\text{C}$  时质量降至 5.75 g 后停止下降。在  $400^\circ\text{C}$  时观察到第二次失重，最终留下 1.50 g 化合物 H，在更高温度下其质量保持不变。

## 1.6 利用热重分析数据确定石头和化合物 H 的化学式。— 4.0 分

## 元素周期表

|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
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| 1                 |  |                   |  |                   |  |                   |  |                   |  |                   |  | 18                |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
| 1<br>H<br>1.008   |  | 2                 |  |                   |  |                   |  |                   |  |                   |  |                   |  | 13                |  | 14                |  | 15                |  | 16                |  | 17                |  | 18<br>He<br>4.003 |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
| 3<br>Li<br>6.94   |  | 4<br>Be<br>9.01   |  |                   |  |                   |  |                   |  |                   |  |                   |  | 5<br>B<br>10.81   |  | 6<br>C<br>12.01   |  | 7<br>N<br>14.01   |  | 8<br>O<br>16.00   |  | 9<br>F<br>19.00   |  | 10<br>Ne<br>20.18 |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
| 11<br>Na<br>22.99 |  | 12<br>Mg<br>24.30 |  |                   |  |                   |  |                   |  |                   |  |                   |  | 13<br>Al<br>26.98 |  | 14<br>Si<br>28.09 |  | 15<br>P<br>30.97  |  | 16<br>S<br>32.06  |  | 17<br>Cl<br>35.45 |  | 18<br>Ar<br>39.95 |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
| 19<br>K<br>39.10  |  | 20<br>Ca<br>40.08 |  | 21<br>Sc<br>44.96 |  | 22<br>Ti<br>47.87 |  | 23<br>V<br>50.94  |  | 24<br>Cr<br>52.00 |  | 25<br>Mn<br>54.94 |  | 26<br>Fe<br>55.85 |  | 27<br>Co<br>58.93 |  | 28<br>Ni<br>58.69 |  | 29<br>Cu<br>63.55 |  | 30<br>Zn<br>65.38 |  | 31<br>Ga<br>69.72 |  | 32<br>Ge<br>72.63 |  | 33<br>As<br>74.92 |  | 34<br>Se<br>78.97 |  | 35<br>Br<br>79.90 |  | 36<br>Kr<br>83.80 |  |  |  |
| 37<br>Rb<br>85.47 |  | 38<br>Sr<br>87.62 |  | 39<br>Y<br>88.91  |  | 40<br>Zr<br>91.22 |  | 41<br>Nb<br>92.91 |  | 42<br>Mo<br>95.95 |  | 43<br>Tc<br>101.1 |  | 44<br>Ru<br>102.9 |  | 45<br>Rh<br>106.4 |  | 46<br>Pd<br>107.9 |  | 47<br>Ag<br>107.9 |  | 48<br>Cd<br>112.4 |  | 49<br>In<br>114.8 |  | 50<br>Sn<br>118.7 |  | 51<br>Sb<br>121.8 |  | 52<br>Te<br>127.6 |  | 53<br>I<br>126.9  |  | 54<br>Xe<br>131.3 |  |  |  |
| 55<br>Cs<br>132.9 |  | 56<br>Ba<br>137.3 |  | 57-71             |  | 72<br>Hf<br>178.5 |  | 73<br>Ta<br>180.9 |  | 74<br>W<br>183.8  |  | 75<br>Re<br>186.2 |  | 76<br>Os<br>190.2 |  | 77<br>Ir<br>192.2 |  | 78<br>Pt<br>195.1 |  | 79<br>Au<br>197.0 |  | 80<br>Hg<br>200.6 |  | 81<br>Tl<br>204.4 |  | 82<br>Pb<br>207.2 |  | 83<br>Bi<br>209.0 |  | 84<br>Po<br>-     |  | 85<br>At<br>-     |  | 86<br>Rn<br>-     |  |  |  |
| 87<br>Fr<br>-     |  | 88<br>Ra<br>-     |  | 89-103            |  | 104<br>Rf<br>-    |  | 105<br>Db<br>-    |  | 106<br>Sg<br>-    |  | 107<br>Bh<br>-    |  | 108<br>Hs<br>-    |  | 109<br>Mt<br>-    |  | 110<br>Ds<br>-    |  | 111<br>Rg<br>-    |  | 112<br>Cn<br>-    |  | 113<br>Nh<br>-    |  | 114<br>Fl<br>-    |  | 115<br>Mc<br>-    |  | 116<br>Lv<br>-    |  | 117<br>Ts<br>-    |  | 118<br>Og<br>-    |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
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|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
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|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
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|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
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|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
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|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
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|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
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|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
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|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
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|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
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|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
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c1ccc2ccccc2c1



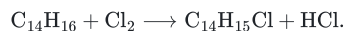
萘由两个稠合的六元芳香环组成。其分子平面，以及分别通过分子长轴和短轴且垂直于分子平面的两个平面，构成三个两两垂直的镜面。

因此，蓝色组分是 **Z**，即化合物 **7**，**母菊萘**，又称 7-乙基-1,4-二甲基萘， $\text{C}_{14}\text{H}_{16}$ ：

CCC1=CC2=C(C)C=CC2=C(C)C=C1

氯化数据独立地证实了这一鉴定结果。相隔两个质量单位且强度比约为 3 : 1 的一对分子离子峰，是含有一个氯原子的特征，分别源于  $^{35}\text{Cl}$  和  $^{37}\text{Cl}$ 。

通过取代反应进行一氯化，得到：



这两种氯同位素分子的标称质量分别为

$$14(12) + 15(1) + 35 = 218,$$

$$14(12) + 15(1) + 37 = 220.$$

这与题述峰完全一致。由这些质量即可确定氯化产物的分子式，无须确定氯的取代位置。

### 1.3

设

$$p = P(^{12}\text{C}) = 0.989, \quad q = P(^{13}\text{C}) = 0.011.$$

对于含有  $n$  个碳原子的分子，不含  $^{13}\text{C}$  原子和恰含一个  $^{13}\text{C}$  原子的概率分别为

$$P_0 = p^n, \quad P_1 = nqp^{n-1}.$$

因此，

$$\frac{I(M+1)}{I(M)} = \frac{P_1}{P_0} = n \frac{q}{p} = \frac{1}{9}.$$

故

$$n = \frac{0.989}{9(0.011)} = 9.9899 \approx \boxed{10}.$$

计算结果与整数的微小偏差来自所给丰度和强度比的舍入。

与铁(III)水溶液产生特征颜色，表明存在**酚基**，其原因是形成了有色的铁-酚盐配合物。化合物 **1** 和 **5** 均含有酚羟基，但只有 **5** 含有十个碳原子。

因此，**W** 是化合物 **5**，即**丁香酚**，又称 2-甲氧基-4-(丙-2-烯-1-基)苯酚， $\text{C}_{10}\text{H}_{12}\text{O}_2$ ：

COc1cc(CC=C)ccc1O

### 1.4

化合物 **D** 是一种钠-金属氟化物。其中氟的质量分数为

$$w_{\text{F}} = 100.00 - 32.85 - 12.85 = 54.30\%.$$

对于 100.00 g 的 **D**，

$$n_{\text{Na}} = \frac{32.85 \text{ g}}{22.99 \text{ g mol}^{-1}} = 1.4289 \text{ mol},$$

$$n_{\text{F}} = \frac{54.30 \text{ g}}{19.00 \text{ g mol}^{-1}} = 2.8579 \text{ mol}.$$

因此， $\text{Na} : \text{F} = 1 : 2$ 。所以，按含一个金属原子写出的化学式为  $\text{Na}_a\text{QF}_{2a}$ ，其中金属的氧化态为  $+a$ 。该金属原子的摩尔质量必须满足

$$\frac{M_{\text{Q}}}{a} = \frac{12.85}{32.85}(22.99) = 8.993 \text{ g mol}^{-1}.$$

当  $a = 3$  时，得到  $M_{\text{Q}} = 26.98 \text{ g mol}^{-1}$ ，由此确定该金属为**铝**。

因此，**Q** 是**铝**，Al，其 SMILES 为 `[Al]`；**D** 是**冰晶石**，即六氟合铝酸钠， $\text{Na}_3\text{AlF}_6$ 。

其摩尔质量为

$$M_{\text{D}} = 3(22.99) + 26.98 + 6(19.00) = 209.95 \text{ g mol}^{-1}.$$

计算得到的质量分数为

$$w_{\text{Na}} = \frac{68.97}{209.95}(100\%) = 32.85\%, \quad w_{\text{Al}} = \frac{26.98}{209.95}(100\%) = 12.85\%.$$

冰晶石在铝的生产中用作熔融电解质介质，与题目给出的工业用途线索一致。

表示其离子组成的 SMILES 为：

`[Na+].[Na+].[Na+].[Al+3].[F-].[F-].[F-].[F-].[F-].[F-]`

冰晶石含有八面体形的  $[\text{AlF}_6]^{3-}$  单元。这种以点分隔的 SMILES 记录的是组成和电荷，并不表示其配位几何构型或晶格。

**C** 是**氟化铝**， $\text{AlF}_3$ ：

`[Al+3].[F-].[F-].[F-]`

由于

$$M_{\text{AlF}_3} = 26.98 + 3(19.00) = 83.98 \text{ g mol}^{-1},$$

由水合物中水的质量分数可得

$$\frac{18.016x}{83.98 + 18.016x} = 0.3916.$$

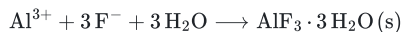
因此,

$$x = \frac{0.3916(83.98)}{0.6084(18.016)} = 3.0003 \approx \boxed{3}.$$

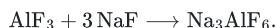
该沉淀是三水合氟化铝,  $\text{AlF}_3 \cdot 3 \text{H}_2\text{O}$ :

[Al+3].[F-].[F-].[F-].O.O.O

相关的配平反应方程式为



和



## 1.5

**E** 是六甲基苯,  $\text{C}_{12}\text{H}_{18}$ :

Cc1c(C)c(C)c(C)c(C)c1C

绘制 **E** 时, 在苯环的每个碳原子上连接一个甲基。这六个等价的取代基使取代模式绕垂直于环平面的轴具有所要求的六重对称性。

其中氢的质量分数为

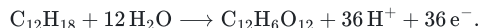
$$w_{\text{H}} = \frac{18(1.008)}{12(12.01) + 18(1.008)}(100\%) = 11.1818\% \approx 11.18\%.$$

将全部六个苄位甲基氧化为羧基, 得到 **F**, 即**苯六甲酸**, 又称**苯六羧酸**,  $\text{C}_6(\text{COOH})_6$ :

O=C(O)c1c(C(=O)O)c(C(=O)O)c(C(=O)O)c(C(=O)O)c1C(=O)O

绘制 **F** 时, 将 **E** 中的每个甲基替换为  $-\text{COOH}$ 。

每个甲基碳原子发生失去六个电子的氧化反应, 因此每个 **E** 分子共失去 36 个电子。配平后的氧化半反应为



将其与酸性条件下高锰酸根的还原半反应合并, 得到

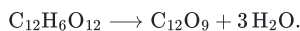


三对相邻羧基脱水, 生成 **G**, 即**苯六甲酸三酐**,  $\text{C}_{12}\text{O}_9$ :

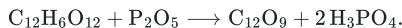
O=C1OC(=O)c2c1c1c(c3c2C(=O)OC3=O)C(=O)OC1=O

绘制 **G** 时, 保留中央苯环, 并使位于 1, 2、3, 4 和 5, 6 位的各对羧基分别形成环状酸酐。每一对羧基形成一个含有  $-\text{C}(=\text{O})-\text{O}-\text{C}(=\text{O})-$  连接片段的五元环, 并与苯环的一条边稠合。旋转  $120^\circ$  可使三个酸酐环相互重合, 因此存在一条垂直于中央环平面的三重对称轴。

从形式上看, **F** 失去三个水分子:



将脱水剂吸收这些水的过程计入后, 配平的总反应为



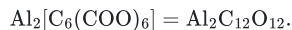
**G** 中氧的质量分数为

$$w_{\text{O}} = \frac{9(16.00)}{12(12.01) + 9(16.00)}(100\%) = 49.9792\% \approx 49.98\%.$$

因此, 元素组成和对称性均与题意相符。

## 1.6

苯六甲酸是六元酸。其完全去质子化的阴离子带有  $6-$  电荷, 因此根据其与铝(III)之间的电荷平衡, 得到无水盐



其摩尔质量为

$$M_{\text{无水盐}} = 2(26.98) + 12(12.01) + 12(16.00) = 390.08 \text{ g mol}^{-1}.$$

第一次失重对应脱水过程:

$$\begin{aligned} m_{\text{水}} &= 10.00 - 5.75 = 4.25 \text{ g}, \\ n_{\text{水}} &= \frac{4.25}{18.016} = 0.2359 \text{ mol}. \end{aligned}$$

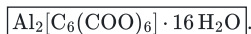
无水盐的物质的量为

$$n_{\text{盐}} = \frac{5.75}{390.08} = 0.0147406 \text{ mol}.$$

因此, 每个化学式单元中水分子的数目为

$$x = \frac{0.235901}{0.0147406} = 16.0036 \approx \boxed{16}.$$

所以, 这块石头是**蜜蜡石**, 即十六水合苯六甲酸铝:

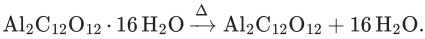


表示其化学式单元组成的 SMILES 为：

[Al+3].[Al+3].O=C([O-])c1c(C(=O)[O-])c(C(=O)[O-])c(C(=O)[O-])c(C(=O)[O-])c1C(=O)[O-].O.O.O.O.O.O.O.O.O.O.O.O.O.O.O.O

这一表示法给出了两个铝离子、苯甲酸根阴离子和十六个水分子，但并未指定它们在固态中的配位方式。

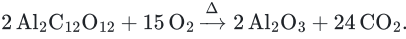
脱水方程式为



在空气中，有机阴离子被氧化，留下 H，即氧化铝， $\text{Al}_2\text{O}_3$ ：

[Al+3].[Al+3].[O-2].[O-2].[O-2]

配平的氧化反应为



因此，

$$M_{\text{Al}_2\text{O}_3} = 2(26.98) + 3(16.00) = 101.96\text{ g mol}^{-1}.$$

利用

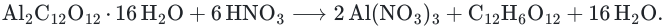
$$M_{\text{石头}} = 390.08 + 16(18.016) = 678.336\text{ g mol}^{-1},$$

可预测 10.00 g 样品在两个阶段的残留物质量分别为

$$m_{\text{无水盐}} = 10.00 \frac{390.08}{678.336} = 5.7505\text{ g} \approx 5.75\text{ g},$$
$$m_{\text{Al}_2\text{O}_3} = 10.00 \frac{101.96}{678.336} = 1.5031\text{ g} \approx 1.50\text{ g}.$$

两者均与实测平台质量一致。第二次失重是净质量损失：氧气从空气中进入，而二氧化碳逸出。

此前在硝酸中的溶解过程也与这一化学式一致：



解答已与官方解答核对。

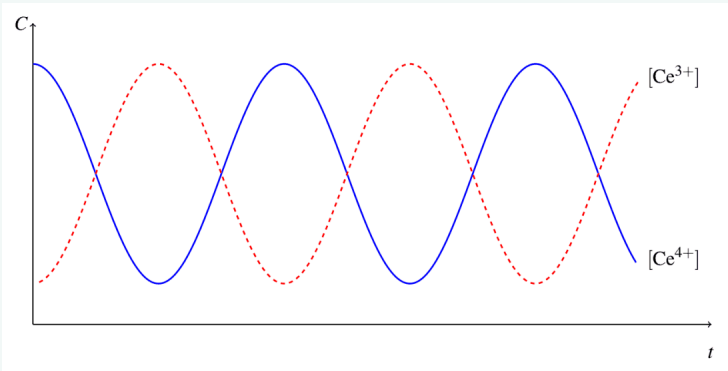
## 题目 2：别洛索夫—扎博京斯基反应的动力学

### T2. 别洛索夫—扎博京斯基反应的动力学

6%

| 2.1 | 2.2 | 2.3 | 2.4 | 2.5 | 2.6 | 2.7 | Σ  |
|-----|-----|-----|-----|-----|-----|-----|----|
| 2   | 11  | 4   | 2   | 9   | 4   | 3   | 35 |

将化学试剂  $\text{KBrO}_3$ 、 $\text{CH}_2(\text{COOH})_2$ （丙二酸，— MA）、 $\text{Ce}(\text{SO}_4)_2$  和  $\text{H}_2\text{SO}_4$  混合后，Ce 各物种的浓度  $C$  发生振荡，溶液的颜色也在黄色（由  $\text{Ce}^{4+}$  引起）与无色（由  $\text{Ce}^{3+}$  引起）之间振荡。示意图如下：



#### 2.1 — 2.0 分

写出 别洛索夫—扎博京斯基反应（BZ 反应）配平后的总反应方程式。注意：在此反应中，MA 被氧化为  $\text{CO}_2$ ， $\text{BrO}_3^-$  被还原为  $\text{Br}^-$ ， $\text{Ce(IV)}$  为催化剂。

BZ 反应的机理如下所示（BMA —  $\text{CHBr}(\text{COOH})_2$ ）：

|           |                                                                                                                                                                                                                                                                                                                       |
|-----------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Process A | $\begin{cases} (1) \text{HBrO}_2 + \text{BrO}_3^- + \text{H}^+ \xrightarrow{k_1} 2\text{BrO}_2 + \text{H}_2\text{O} \\ (2) \text{BrO}_2 + \text{Ce}^{3+} + \text{H}^+ \xrightarrow{k_2} \text{HBrO}_2 + \text{Ce}^{4+} \\ (3) 2\text{HBrO}_2 \xrightarrow{k_3} \text{BrO}_3^- + \text{HBrO} + \text{H}^+ \end{cases}$ |
| Process B | $\begin{cases} (4) \text{HBrO}_2 + \text{Br}^- + \text{H}^+ \xrightarrow{k_4} 2\text{HBrO} \\ (5) \text{BrO}_3^- + \text{Br}^- + 2\text{H}^+ \xrightarrow{k_5} \text{HBrO} + \text{HBrO}_2 \\ (6) \text{HBrO} + \text{MA} \xrightarrow{k_6} \text{BMA} + \text{H}_2\text{O} \end{cases}$                              |
| Process C | $(7) \text{Ce}^{4+} + \text{BMA} \xrightarrow{k_7} \text{Ce}^{3+} + \text{Br}^- + \text{other products}$                                                                                                                                                                                                              |

|                                                       |
|-------------------------------------------------------|
| $k_1 = 1.0 \times 10^4 \text{ M}^{-2} \text{ s}^{-1}$ |
| $k_2 = 6.2 \times 10^4 \text{ M}^{-2} \text{ s}^{-1}$ |
| $k_3 = 4.0 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ |
| $k_4 = 2.0 \times 10^9 \text{ M}^{-2} \text{ s}^{-1}$ |
| $k_5 = 2.1 \text{ M}^{-3} \text{ s}^{-1}$             |
| $k_6 = 8.2 \text{ M}^{-1} \text{ s}^{-1}$             |
| $k_7 = 1.0 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$ |

在 BZ 反应中，过程 C 持续进行，而过程 A 和 B 交替进行。

假设：

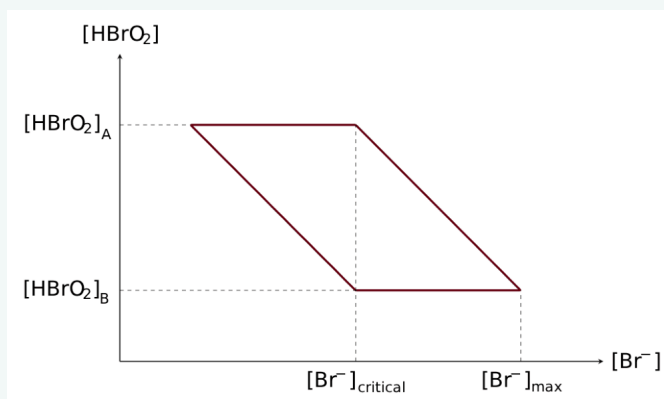
- 过程 A 进行时，溶液呈黄色，且过程 B 几乎不发生；
- 过程 B 进行时，溶液呈无色，且过程 A 几乎不发生；
- $[\text{BrO}_3^-]_0 = 0.06 \text{ M}$ 、 $[\text{MA}]_0 = 0.1 \text{ M}$ 、 $[\text{H}^+]_0 = 0.8 \text{ M}$ 、 $[\text{Ce}^{4+}]_0 = 0.001 \text{ M}$ ；
- 在整个 BZ 反应过程中，反应物（ $\text{Ce}^{4+}$  除外）的浓度和 pH 均保持恒定。

## 2.2 — 11.0 分

利用稳态近似，计算  $\text{HBrO}_2$  在过程 A 和 B 中的稳态摩尔浓度  $[\text{HBrO}_2]_A$  和  $[\text{HBrO}_2]_B$ 。

若未能计算出  $[\text{HBrO}_2]_A$  和  $[\text{HBrO}_2]_B$ ，可在后续计算中使用  $[\text{HBrO}_2]_A = 1 \times 10^{-5} \text{ M}$  和  $[\text{HBrO}_2]_B = 1 \times 10^{-10} \text{ M}$ 。

在 BZ 反应过程中， $\text{HBrO}_2$  和  $\text{Br}^-$  的浓度振荡具有严格的相互关系，如下方  $[\text{HBrO}_2]$  对  $[\text{Br}^-]$  的相图所示：



其中， $[\text{Br}^-]_{\max}$  为  $\text{Br}^-$  的最大浓度， $[\text{Br}^-]_{\text{critical}}$  为过程从 A 切换至 B 或从 B 切换至 A 时  $\text{Br}^-$  的临界浓度。要使过程 A 切换至过程 B，基元步骤 (4) 的反应速率必须超过基元步骤 (1) 的反应速率，反之亦然。

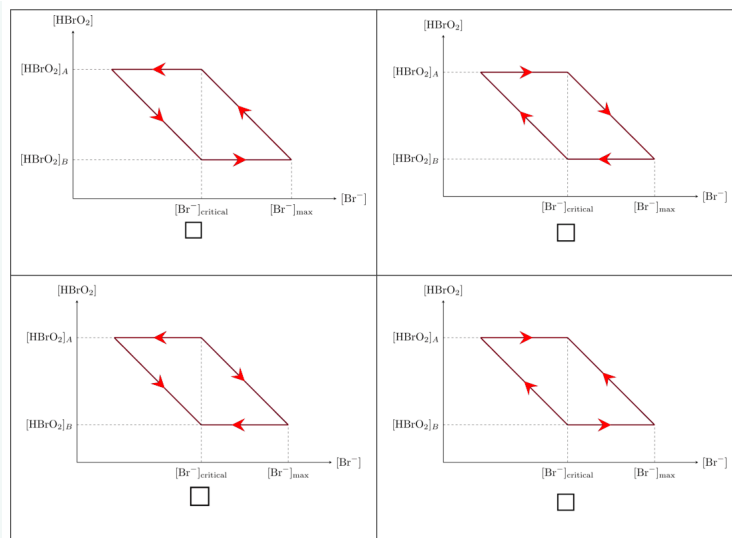
## 2.3 — 4.0 分

计算  $[\text{Br}^-]_{\text{critical}}$ 。

若未能计算出  $[\text{Br}^-]_{\text{critical}}$ ，请在后续计算中使用  $[\text{Br}^-]_{\text{critical}} = 1 \times 10^{-7} \text{ M}$ 。

## 2.4 — 2.0 分

随着时间推移， $[\text{HBrO}_2]$  和  $[\text{Br}^-]$  的浓度将在  $[\text{HBrO}_2]$  对  $[\text{Br}^-]$  的相图中沿哪个方向变化？在正确的方框内打勾。



体系并非以恒定速度沿  $[\text{HBrO}_2]$  对  $[\text{Br}^-]$  的相图运动，即  $[\text{Br}^-]$  的浓度从  $[\text{Br}^-]_{\text{max}} = 7.0 \times 10^{-4} \text{ M}$  缓慢降低至  $[\text{Br}^-]_{\text{critical}}$ ，随后几乎立即再次达到  $[\text{Br}^-]_{\text{max}}$ 。

2.5 — 9.0 分

根据所给数据，计算 BZ 反应的振荡周期  $\tau$ ，单位为秒。

2.6 — 4.0 分

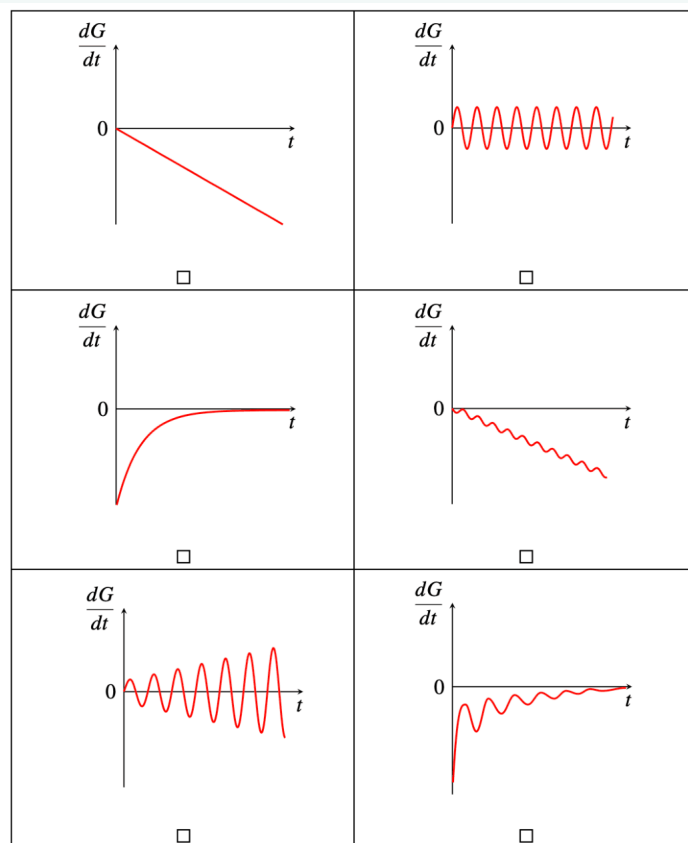
对正在发生 BZ 反应的开放体系进行以下操作 (1–4)，会产生什么影响？每种情况仅在 (a–e) 中的一个方框内打勾。

1. 在过程 A 期间加入少量  $\text{Ce}^{4+}$ 。
2. 在过程 B 期间加入少量  $\text{Ag}^+$ 。
3. 在过程 B 期间加入少量  $\text{Br}^-$ 。
4. 持续加入  $\text{Br}^-$ 。

- [ a ] 延长过程 A  
[ b ] 延长过程 B  
[ c ] 过程 A 切换至过程 B  
[ d ] 过程 B 切换至过程 A  
[ e ] 振荡停止

2.7 — 3.0 分

哪幅图定性地表示了发生振荡反应的封闭体系中吉布斯能的变化速率 ( $\frac{dG}{dt}$ )？在正确的方框内打勾。



题目译自官方英文原文。

## 答案

- 2.1:  $3\text{CH}_2(\text{COOH})_2 + 4\text{BrO}_3^- \longrightarrow 9\text{CO}_2 + 4\text{Br}^- + 6\text{H}_2\text{O}$ 。
- 2.2:  $[\text{HBrO}_2]_{\text{A}} = \boxed{6.0 \times 10^{-6} \text{ M}}$ ;  $[\text{HBrO}_2]_{\text{B}} = \boxed{5.0 \times 10^{-11} \text{ M}}$ 。
- 2.3:  $[\text{Br}^-]_{\text{critical}} = \boxed{3.0 \times 10^{-7} \text{ M}}$ 。
- 2.4: 答题纸中 2.4 配图的右上图: 沿顺时针方向运动。
- 2.5:  $\tau \approx 48 \text{ s}$ 。
- 2.6: 预期选项为: 1-c; 2-d; 3-b; 4-e, 前提是扰动强度足够大, 具体解释见下文。
- 2.7: 答题纸中 2.7 配图的右下图:  $dG/dt$  在零以下作阻尼振荡并趋近于零。

## 解答

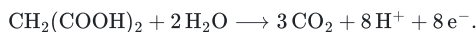
下文所用物种的名称和 SMILES 如下。

| 物种                                 | 名称       | SMILES                         |
|------------------------------------|----------|--------------------------------|
| $\text{CH}_2(\text{COOH})_2$ , MA  | 丙二酸      | <chem>O=C(O)CC(=O)O</chem>     |
| $\text{CHBr}(\text{COOH})_2$ , BMA | 溴丙二酸     | <chem>O=C(O)C(Br)C(=O)O</chem> |
| $\text{BrO}_3^-$                   | 溴酸根离子    | <chem>[O-][Br](=O)=O</chem>    |
| $\text{Br}^-$                      | 溴离子      | <chem>[Br-]</chem>             |
| $\text{HBrO}_2$                    | 亚溴酸      | <chem>O[Br]=O</chem>           |
| $\text{HBrO}$                      | 次溴酸      | <chem>OBr</chem>               |
| $\text{BrO}_2^\bullet$             | 二氧化溴自由基  | <chem>O=[Br]=O</chem>          |
| $\text{CO}_2$                      | 二氧化碳     | <chem>O=C=O</chem>             |
| $\text{H}_2\text{O}$               | 水        | <chem>O</chem>                 |
| $\text{H}^+$                       | 氢离子 (质子) | <chem>[H+]</chem>              |
| $\text{Ce}^{4+}$                   | 铈(IV)离子  | <chem>[Ce+4]</chem>            |
| $\text{Ce}^{3+}$                   | 铈(III)离子 | <chem>[Ce+3]</chem>            |
| $\text{Ag}^+$                      | 银(I)离子   | <chem>[Ag+]</chem>             |
| $\text{AgBr}$                      | 溴化银      | <chem>[Ag+].[Br-]</chem>       |

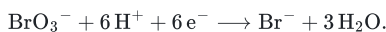
溴化银的 SMILES 表示其组成离子, 而非固体的晶格结构。这些离子的 SMILES 未表示溶剂化。

### 2.1

一个丙二酸分子完全氧化为三个二氧化碳分子时, 释放八个电子:



溴酸根离子还原为溴离子时, 消耗六个电子:



将氧化半反应乘以 3, 还原半反应乘以 4. 消去 24 个电子、24 个氢离子以及两边共有的水, 得到



铈在其氧化态之间循环转化并得到再生, 因此不出现在净反应方程式中。

### 2.2

定义

$$\begin{aligned} x &= [\text{HBrO}_2], & r &= [\text{BrO}_2^\bullet], & b &= [\text{Br}^-], \\ a &= [\text{BrO}_3^-] = 0.06 \text{ M}, & h &= [\text{H}^+] = 0.8 \text{ M}. \end{aligned}$$

令  $v_i$  表示基元步骤  $i$  的反应速率, 化学计量因子在各物种的衡算式中另行计入。

对于过程 A,

$$v_1 = k_1 x a h, \quad v_2 = k_2 r [\text{Ce}^{3+}] h, \quad v_3 = k_3 x^2.$$

对二氧化溴自由基应用稳态近似, 得到

$$\frac{dr}{dt} = 2v_1 - v_2 \simeq 0 \implies v_2 = 2v_1.$$

亚溴酸的衡算式为

$$\frac{dx}{dt} = -v_1 + v_2 - 2v_3 \simeq 0.$$

$v_3$  前的因子 2 必不可少: 步骤 (3) 每发生一次, 就消耗两个亚溴酸分子。代入  $v_2 = 2v_1$ , 得

$$k_1 x a h - 2k_3 x^2 = 0.$$

因此, 对应于正在进行的过程 A 的非零稳态浓度为

$$x_{\text{A}} = \frac{k_1 a h}{2k_3}.$$

代入数值得

$$x_A = \frac{(1.0 \times 10^4 \text{ M}^{-2}\text{s}^{-1})(0.06 \text{ M})(0.8 \text{ M})}{2(4.0 \times 10^7 \text{ M}^{-1}\text{s}^{-1})} = \boxed{6.0 \times 10^{-6} \text{ M}}.$$

对于过程 B，步骤 (5) 生成亚溴酸，步骤 (4) 消耗亚溴酸：

$$v_4 = k_4 x b h, \quad v_5 = k_5 a b h^2.$$

因此

$$\frac{dx}{dt} = v_5 - v_4 \simeq 0,$$

约去非零因子  $b$  和  $h$ ，得

$$x_B = \frac{k_5 a h}{k_4}.$$

于是

$$x_B = \frac{(2.1 \text{ M}^{-3}\text{s}^{-1})(0.06 \text{ M})(0.8 \text{ M})}{2.0 \times 10^9 \text{ M}^{-2}\text{s}^{-1}} = 5.04 \times 10^{-11} \text{ M} \approx \boxed{5.0 \times 10^{-11} \text{ M}}.$$

### 2.3

在切换阈值处，步骤 (1) 和 (4) 的速率相等：

$$k_1 x a h = k_4 x b_{\text{critical}} h.$$

约去  $x$  和  $h$ ，得

$$b_{\text{critical}} = \frac{k_1 a}{k_4} = \frac{1.0 \times 10^4}{2.0 \times 10^9} (0.06 \text{ M}) = \boxed{3.0 \times 10^{-7} \text{ M}}.$$

低于此浓度时，步骤 (1) 占主导，有利于过程 A 进行。高于此浓度时，步骤 (4) 占主导，有利于过程 B 进行。

### 2.4

在过程 A 期间，溶液中含有相当量的铈(IV)，因此过程 C 生成溴离子。溴离子浓度沿上方分支增加，直至体系切换至过程 B。

在过程 B 期间，溴离子被消耗，而亚溴酸浓度保持在较低水平。体系沿下方分支向左移动，直至溴离子浓度降至切换阈值，过程 A 重新开始。

因此，箭头必须指向：

- 沿上方水平边向右；
- 沿右侧斜边向右下方；
- 沿下方水平边向左；
- 沿左侧斜边向左上方。

这就是沿顺时针方向运动，如答题纸中 2.4 配图的右上图所示。

### 2.5

振荡周期主要由过程 B 期间溴离子浓度缓慢降低所需的时间决定。随后恢复至最大浓度所需的时间视为可以忽略。

在 B 期间，完整的溴离子衡算式为

$$\frac{db}{dt} = -v_4 - v_5 + v_7.$$

按照题目预期采用的近似，无色的 B 阶段中铈(IV) 的含量极少，因此在这一缓慢阶段忽略

$$v_7 = k_7 [\text{Ce}^{4+}] [\text{BMA}]$$

这一项。由稳态计算可知， $v_4 = v_5$ 。因此，

$$\frac{db}{dt} \simeq -2v_5 = -2k_5 a h^2 b.$$

步骤 (4) 和 (5) 都消耗溴离子；因子 2 由此而来。

有效一级衰减速率常数为

$$k_{\text{eff}} = 2k_5 a h^2 = 2(2.1 \text{ M}^{-3}\text{s}^{-1})(0.06 \text{ M})(0.8 \text{ M})^2 = 0.16128 \text{ s}^{-1}.$$

积分得

$$b(t) = b_{\text{max}} e^{-k_{\text{eff}} t}.$$

令  $b(\tau) = b_{\text{critical}}$ ，得

$$\tau \simeq \frac{1}{k_{\text{eff}}} \ln \left( \frac{b_{\text{max}}}{b_{\text{critical}}} \right).$$

因此

$$\tau = \frac{\ln \left( \frac{7.0 \times 10^{-4}}{3.0 \times 10^{-7}} \right)}{0.16128 \text{ s}^{-1}} = 48.0844 \text{ s} \approx \boxed{48 \text{ s}}.$$

### 2.6

#### 1. 在过程 A 期间加入铈(IV)：(c)。

增大  $[\text{Ce}^{4+}]$  会加快过程 C，从而加快溴离子的生成。若这使溴离子浓度升高并超过临界浓度，步骤 (4) 的速率就会超过步骤 (1)，于是过程 A 切换至过程 B。

2. 在过程 B 期间加入银(I): (d)。

银(I) 通过沉淀反应除去溴离子:



若溴离子浓度降至临界浓度以下, 步骤 (1) 就会占主导, 于是过程 B 切换至过程 A。

3. 在过程 B 期间加入溴离子: (b)。

溴离子浓度升高, 与切换阈值的差距增大。将其消耗至该阈值所需的时间更长, 因此加入溴离子会延长过程 B。

4. 持续加入溴离子: (e)。

以足够的速率持续供给溴离子, 可使其浓度保持在临界浓度以上, 从而维持过程 B 并阻止交替切换。振荡停止。

## 2.7

对于恒温恒压下发生自发反应的封闭体系,

$$\frac{dG}{dt} \leq 0.$$

浓度可以发生振荡, 吉布斯能降低的速率也可以变化, 但吉布斯能本身始终在降低。当体系趋近平衡时,

$$\frac{dG}{dt} \longrightarrow 0.$$

因此, 预期的图像应显示  $dG/dt$  始终在零以下振荡, 且随着曲线趋近于零, 振幅逐渐减小: 即答题纸中 2.7 配图的右下图。

解答已与官方解答核对。

## 题目 3: 走进网状化学

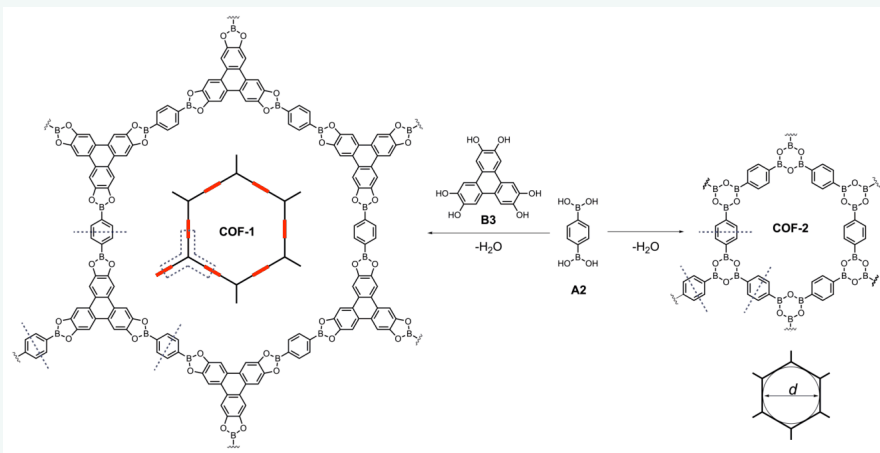
### T3. 走进网状化学

7%

| 3.1 | 3.2 | 3.3 | 3.4 | 3.5 | 3.6 | 3.7 |  $\sum$  | |---:|---:|---:|---:|---:|---:|---:|---:| | 2 | 3 | 23 | 12 | 6 | 12 | 5 | 63 |

共价有机框架 (COF) 是一类聚合物, 有机前体通过反应形成共价键, 构筑二维或三维结构, 从而得到多孔晶态材料。下图展示了由硼酸酯和硼氧六环形成的蜂窝型二维 COF 的两个例子 (重复单元用虚线标出)。

所有 COF 拓扑结构图中的黑色和红色粗线代表不同的构筑单元。

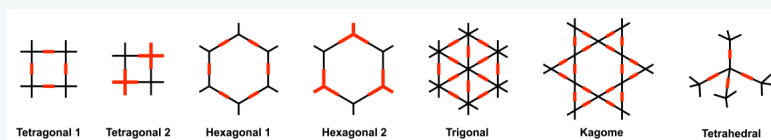
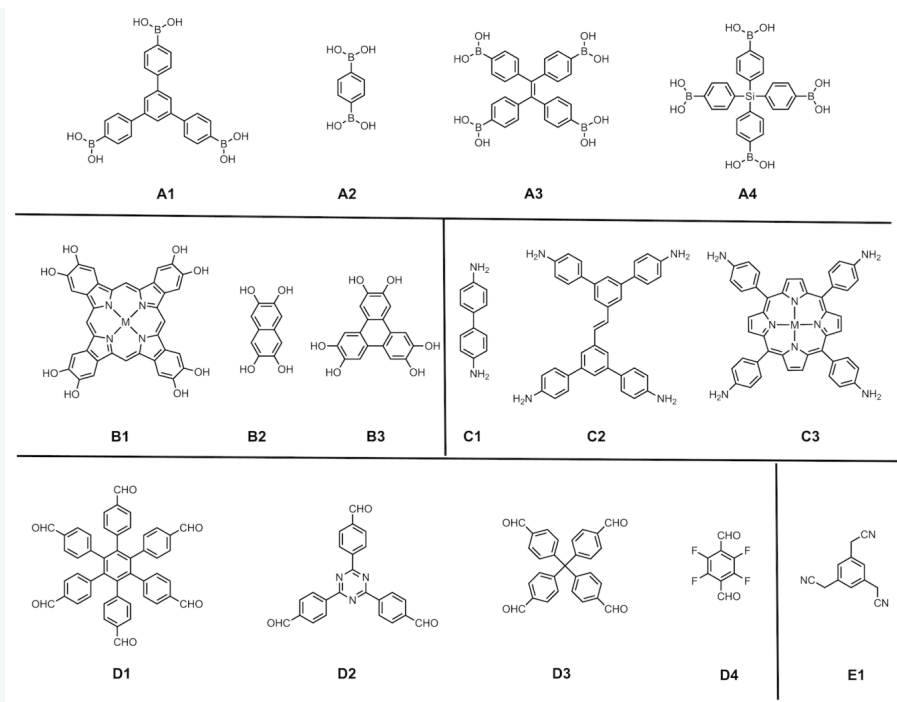


3.1 确定 COF-1 的最简式, 并计算 COF-1 中碳的质量百分数 (% , 保留两位小数)。2.0 分

3.2 根据以下假设, 计算 COF-2 蜂窝的内径  $d$ , 单位为 Å: 3.0 分

- $\text{C}-\text{C}/\text{C}=\text{C}$  (芳烃) = 1.39 Å
- $\text{C}-\text{B}$  = 1.56 Å
- $\text{B}-\text{O}$  = 1.38 Å
- 注意, 六边形内切圆的直径  $d$  为  $d = \sqrt{3}a$ , 其中  $a$  为六边形的边长。
- 忽略连接体的宽度。

下列结构可以形成二维和三维 COF。本题仅考虑通过缩合反应形成含有硼酸酯、亚胺及  $\text{C}=\text{C}$  键的 COF。A-E 代表具有不同官能团的化合物类别。

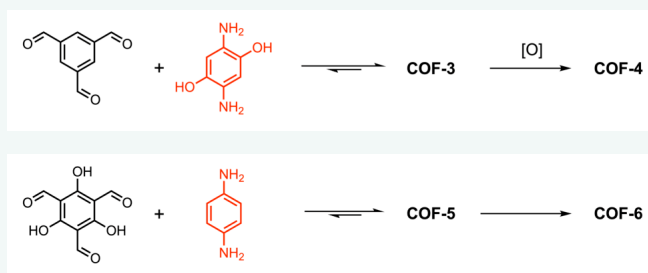


Tetragonal 表示四方形，Hexagonal 表示六方形，Trigonal 表示三角形，Kagome 表示笼目形，Tetrahedral 表示四面体形。

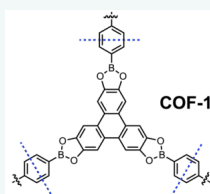
3.3 在表格的所有空白单元格中填写能形成上述拓扑结构的其他单体组合示例；若你确定没有其他组合满足该拓扑结构，则填写“XXX”。所填组合和“XXX”均计分。错误答案（包括组合和“XXX”）将被扣分。空白单元格不计分。23.0 分

| 四方形 1 | 四方形 2 | 六方形 1   | 六方形 2   | 三角形 | 笼目形     | 四面体形 |
|-------|-------|---------|---------|-----|---------|------|
| ■     | ■     | A2 + B3 | E1 + D2 | ■   | C2 + D4 | ■    |
|       |       |         |         |     |         |      |
|       |       |         |         |     |         |      |

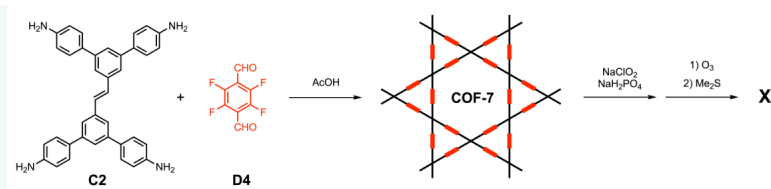
亚胺基 COF 虽然易于合成，但在强酸和强碱条件下也容易水解。在醛或胺单体中引入羟基可以克服这一问题。COF-3 的红外光谱中含有对应于亚胺官能团的伸缩振动吸收带，而 COF-4 中没有。COF-4 含有另一种类型的 C=N 键，元素分析表明，与 COF-3 相比，唯一的变化是每个重复单元额外失去了六个氢原子。COF-5 不可逆地异构化为 COF-6，后者的红外光谱中没有亚胺伸缩振动吸收带。



3.4 画出 COF 3-6 的重复单元。用虚线标明各重复单元的边界，如下方 COF-1 所示。12.0 分

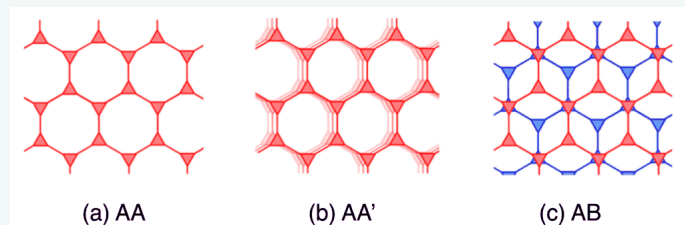


大环化合物 X 由 COF-7 (C2 + D4) 经合成后修饰，再经降解制得。

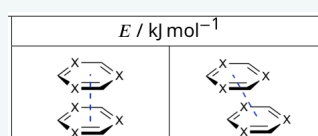


3.5 画出大环化合物 X 的最小重复单元。6.0 分

$\pi-\pi$  相互作用使 COF 层形成不同的堆积模式，其中一些如下所示。

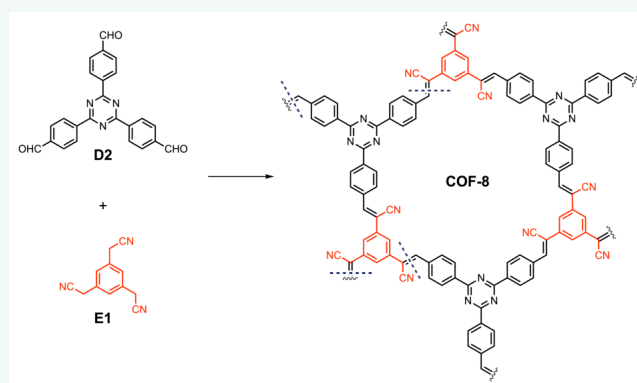


相互作用能可随堆积几何构型而变化，如下所示。



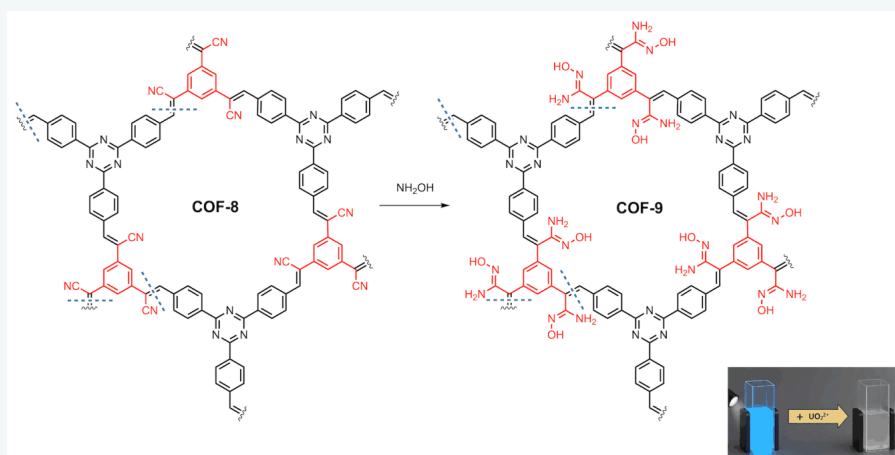
| 相互作用几何构型                        | $E/\text{kJ mol}^{-1}$ | $E/\text{kJ mol}^{-1}$ |
|---------------------------------|------------------------|------------------------|
| 苯 ( $X = \text{CH}$ ) - 苯 (b-b) | -7.9                   | -12.6                  |
| 苯-三嗪 ( $X = \text{N}$ ) (b-t)   | -49.8                  | -55.6                  |
| 三嗪-三嗪 (t-t)                     | -6.7                   | -16.7                  |

由 (E1 + D2) 合成的 COF-8 以其出色的稳定性而著称。COF-8 双层结构采用略微错位的 AA' 模式时，一个重复单元的两层之间的  $\pi-\pi$  堆积相互作用能为  $-67.1 \text{ kJ mol}^{-1}$ 。



3.6 计算 COF-8 在 AA、AB 和 AA' 排列中，一个重复单元的两层之间的  $\pi-\pi$  堆积能。假设  $\pi-\pi$  堆积仅发生在芳香单元之间。12.0 分

由 COF-8 得到的 COF-9 吸附  $\text{UO}_2^{2+}$  离子后会失去荧光。在一项实验中，将 5.000 mg COF-9 悬浮于  $19.90 \text{ mg dm}^{-3}$  的  $\text{UO}_2^{2+}$  溶液 (200.0 mL) 中，达到平衡后过滤。  $\text{UO}_2^{2+}$  的最终浓度为  $9.225 \text{ mg dm}^{-3}$ 。



元素周期表

题目译自官方英文原文。

- 3.1: 最简式为  $\text{C}_9\text{H}_4\text{BO}_2$ ; 碳的质量百分数为 69.77%。
- 3.2:  $d = 15.00 \text{ \AA}$ 。
- 3.3: 两个空白行填写如下:

- **3.4:** COF-3: 羟基取代的亚胺框架; COF-4: 苯并双噁唑框架; COF-5: 烯醇-亚胺框架; COF-6:  $\beta$ -酮烯胺框架。它们的确切连接方式、SMILES 片段及重复单元边界见下文。
- **3.5:** 最小重复单元含有一个 **3,5-双(4-氨基苯基)苯甲醛衍生物单元**和一个**四氟对苯二甲酰基单元**, 二者通过酰胺键连接。其分子式为  $C_{27}H_{14}F_4N_2O_3$ , 带连接位点的 SMILES 为 [\*:1]Nc1ccc(cc1)-c1cc(C=O)cc(c1)-c1ccc(cc1)NC(=O)c1c(F)c(F)c(c(F)c1F)C(=O)[\*:2]。
- **3.6:** 每对重复单元的能量为  $E_{AA} = -38.3, E_{AB} = -49.8, E_{AB'} = -55.6 \text{ kJ mol}^{-1}$ 。
- **3.7:**  $q_e = 427.0 \text{ mg g}^{-1}$ ; 每个孔约有一个  $UO_2^{2+}$  离子。

在下列结构 SMILES 中,  $[*]$  表示与框架其余部分的连接。这些表示的是有限的结构片段: 普通 SMILES 本身并不指定无限周期框架或其虚线重复单元边界。缩合反应中消去的水的 SMILES 为  $O$ 。

单体为：

- 每个 B3 分子含有三个邻苯二酚基团, 而 A2 含有两个硼酸基团。因此, 它们的化学计量比为

每形成一个环状硼酸酯，就消去两个水分子。因此，形成六处这样的连接可得



此处的产物化学式表示框架的组成，而非独立的分子。将各下标除以六，得到



使用题目提供的原子质量，

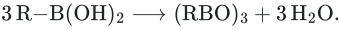
$$M = 9(12.01) + 4(1.008) + 10.81 + 2(16.00) = 154.932 \text{ g mol}^{-1}.$$

因此，

$$w_{\text{C}} = \frac{9(12.01)}{154.932} \times 100\% = \boxed{69.77\%}.$$

### 3.2 — COF-2 的内径

COF-2 含有**硼氧六环**节点，其取代环可表示为  $[\text{*}] \text{B1OB}([\text{*}]) \text{OB}([\text{*}]) \text{O1}$ 。其形成遵循以下配平的缩合反应：



将硼氧六环视为图中所画的正六边形，其中心至硼原子的距离等于边长，即 1.38 Å。正六边形苯环中相对的两个碳原子之间的距离为边长的两倍。

因此，相邻两个硼氧六环中心之间的距离，即蜂窝的边长，为

$$\begin{aligned} a &= 2r_{\text{B-O}} + 2r_{\text{C-B}} + 2r_{\text{C-C}} \\ &= 2(1.38) + 2(1.56) + 2(1.39) \\ &= 8.66 \text{ Å}. \end{aligned}$$

按题意忽略连接体的宽度，

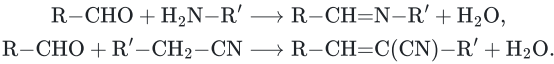
$$d = \sqrt{3}a = \sqrt{3}(8.66) = \boxed{15.00 \text{ Å}}.$$

### 3.3 — 单体组合与拓扑结构

允许的互补官能团组合为：

| 组合    | 形成的连接结构 | 缩合反应的化学计量关系               |
|-------|---------|---------------------------|
| A + B | 环状硼酸酯   | 一个硼酸基团与一个邻苯二酚基团反应，消去两个水分子 |
| C + D | 亚胺      | 一个氨基与一个醛基反应，消去一个水分子       |
| E + D | 氰基取代的烯烃 | 一个活化亚甲基与一个醛基反应，消去一个水分子    |

后两种反应可写为



题图中理想化的连接几何构型为：

| 连接几何构型         | 单体             |
|----------------|----------------|
| 线形，两个连接位点      | A2, B2, C1, D4 |
| 三角形，三个连接位点     | A1, B3, D2, E1 |
| 正方形，四个连接位点     | B1, C3         |
| 适合笼目排列的四连接位点构型 | A3, C2         |
| 平面形，六个连接位点     | D1             |
| 四面体形，四个连接位点    | A4, D3         |

由此得到填写完整的表格：

| 四边形 1   | 四边形 2 | 六方形 1   | 六方形 2   | 三角形     | 笼目形     | 四面体形    |
|---------|-------|---------|---------|---------|---------|---------|
| ■       | ■     | A2 + B3 | E1 + D2 | ■       | C2 + D4 | ■       |
| A2 + B1 | XXX   | A1 + B2 | A1 + B3 | C1 + D1 | A3 + B2 | A4 + B2 |
| C3 + D4 | XXX   | C1 + D2 | XXX     | XXX     | XXX     | C1 + D3 |

这些归属直接由几何构型得出：

- 四边形 1：** 正方形节点通过线形连接体连接。
- 四边形 2：** 需要两种颜色的互补正方形节点。题目提供的单体配对均不满足这一要求：A3 具有笼目型连接几何构型，而 D3 为四面体形。
- 六方形 1：** 三角形节点通过线形连接体连接。
- 六方形 2：** 互补的三角形节点交替排列。
- 三角形：** 六连接的 D1 节点通过线形 C1 连接体相连。
- 笼目形：** A3 和 C2 提供适当的四连接几何构型；与之相容的线形单体分别为 B2 和 D4。
- 四面体形：** 四面体形 A4 或 D3 节点通过相容的线形连接体相连。

E1 + D4 是另一种可行的六方形 1 组合；上面填入的两个新示例已占满其可用单元格。

为完整起见，下表列出了上述归属中所用单体的名称及其 SMILES。A2 和 B3 已在 3.1 中给出。

| 标号 | 名称                   | SMILES                                                                              |
|----|----------------------|-------------------------------------------------------------------------------------|
| A1 | 1,3,5-三(4-硼酸基苯基)苯    | <chem>c1(-c2ccc(B(O)O)cc2)cc(-c2ccc(B(O)O)cc2)cc(-c2ccc(B(O)O)cc2)c1</chem>         |
| A3 | 1,1,2,2-四(4-硼酸基苯基)乙烯 | <chem>C(=C(c1ccc(B(O)O)cc1)c1ccc(B(O)O)cc1)(c1ccc(B(O)O)cc1)c1ccc(B(O)O)cc1</chem>  |
| A4 | 四(4-硼酸基苯基)硅烷         | <chem>[Si](c1ccc(B(O)O)cc1)(c1ccc(B(O)O)cc1)(c1ccc(B(O)O)cc1)c1ccc(B(O)O)cc1</chem> |

| 标号 | 名称                                    | SMILES                                                                                                                     |
|----|---------------------------------------|----------------------------------------------------------------------------------------------------------------------------|
| B1 | 外围带有四个邻苯二酚基团的金属酞菁                     | 自由碱配体: <chem>Oc1cc2c(cc1O)-c1nc-2nc2[nH]c(nc3nc(nc4[nH]c(n1)c1cc(O)c(O)cc41)-c1cc(O)c(O)cc1-3)c1cc(O)c(O)cc21</chem>       |
| B2 | 萘-2,3,6,7-四醇                          | <chem>Oc1cc2cc(O)c(O)cc2cc1O</chem>                                                                                        |
| C1 | 联苯-4,4'-二胺, 即联苯胺                      | <chem>Nc1ccc(-c2ccc(N)cc2)cc1</chem>                                                                                       |
| C2 | ( <i>E</i> )-1,2-双[3,5-双(4-氨基苯基)苯基]乙烯 | <chem>Nc1ccc(-c2cc(-c3ccc(N)cc3)cc(/C=C/c3cc(-c4ccc(N)cc4)cc(-c4ccc(N)cc4)c3)c2)cc1</chem>                                 |
| C3 | 金属 meso-四(4-氨基苯基)卟啉                   | 自由碱配体: <chem>Nc1ccc(-c2c3nc(c(-c4ccc(N)cc4)c4ccc([nH]4)c(-c4ccc(N)cc4)c4nc(c(-c5ccc(N)cc5)c5ccc2[nH]5)C=C4)C=C3)cc1</chem> |
| D1 | 六(4-甲酰基苯基)苯                           | <chem>c1(-c2ccc(C=O)cc2)c(-c2ccc(C=O)cc2)c(-c2ccc(C=O)cc2)c(-c2ccc(C=O)cc2)c(-c2ccc(C=O)cc2)c1-c1ccc(C=O)cc1</chem>        |
| D2 | 2,4,6-三(4-甲酰基苯基)-1,3,5-三嗪             | <chem>O=Cc1ccc(-c2nc(-c3ccc(C=O)cc3)nc(-c3ccc(C=O)cc3)n2)cc1</chem>                                                        |
| D3 | 四(4-甲酰基苯基)甲烷                          | <chem>C(c1ccc(C=O)cc1)(c1ccc(C=O)cc1)(c1ccc(C=O)cc1)c1ccc(C=O)cc1</chem>                                                   |
| D4 | 2,3,5,6-四氟苯-1,4-二甲醛                   | <chem>O=Cc1c(F)c(F)c(C=O)c(F)c1F</chem>                                                                                    |
| E1 | 1,3,5-三(氰甲基)苯                         | <chem>N#CCc1cc(CC#N)cc(CC#N)c1</chem>                                                                                      |

对于 B1 和 C3, 图中没有指明金属  $M$ 。因此, 所列 SMILES 描述的是它们的自由碱配体。在图示金属配合物中, 金属化时两个内侧 N-H 质子被取代,  $M$  与近似平面的  $N_4$  配位腔中四个朝内的氮原子配位。

### 3.4 — COF 3-6 的重复单元

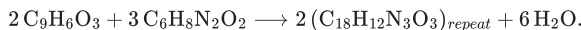
另外用到的起始化合物为:

| 名称                   | 分子式            | SMILES                                    |
|----------------------|----------------|-------------------------------------------|
| 苯-1,3,5-三甲醛          | $C_9H_6O_3$    | <chem>O=Cc1cc(C=O)cc(C=O)c1</chem>        |
| 2,5-二氨基苯-1,4-二醇      | $C_6H_8N_2O_2$ | <chem>Nc1c(O)cc(N)c(O)c1</chem>           |
| 2,4,6-三羟基苯-1,3,5-三甲醛 | $C_9H_6O_6$    | <chem>O=Cc1c(O)c(C=O)c(O)c(C=O)c1O</chem> |
| 苯-1,4-二胺             | $C_6H_8N_2$    | <chem>Nc1ccc(N)cc1</chem>                 |

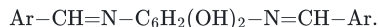
绘制每个所要求的重复单元时, 在中间放置一个完整的三连接中心节点, 画出与其连接的三个连接体, 并画出穿过各连接体中央苯环中部的虚线边界。这样, 每个重复单元包含一个节点和三个半连接体, 与题目所给的 COF-1 示例相同。

#### COF-3: 羟基取代的亚胺框架

缩合反应在每个中心苯节点处形成三个亚胺连接:



中心苯节点之间的每个完整连接体为



两个通过亚胺氮连接的取代基在连接体的环上互为对位; 每个保留的羟基均位于一个亚胺氮取代基的邻位。

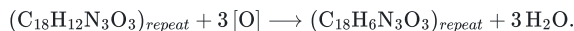
- 三连接苯节点: [\*:1]c1cc([\*:2])cc([\*:3])c1
- 羟基取代的双亚胺连接体: [\*:1]/C=N/c1c(O)cc(/N=C/[\*:2])c(O)c1

斜线表示伸展的亚胺构型。重复单元的组成为  $C_{18}H_{12}N_3O_3$ 。

#### COF-4: 苯并双噁唑框架

每个邻羟基亚胺都发生氧化环化。酚氧原子与相邻的亚胺碳原子成键, 形成耦合的五元 1,3-噁唑环。

在每个位点, 净结果是失去亚胺碳上的氢和酚羟基上的氢。因此, 每个重复单元的三个位点共脱去六个氢原子:



这里的  $[O]$  表示一个氧化用氧当量。

中心的三连接苯节点保持不变。每个连接体变为一个在两条相对边上各耦合一个噁唑环的苯环:

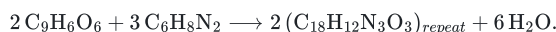
- 苯并双(1,3-噁唑)连接体: [\*:1]c1nc2cc3oc([\*:2])nc3cc2o1

两个外部连接位点均位于各自噁唑环中 O 与 N 之间的碳原子上。

这解释了所有观测结果: 没有失去氧或氮, 每个重复单元恰好失去六个氢, 而剩余的  $C=N$  键属于芳香性噁唑环, 并非普通亚胺基团。

#### COF-5: 烯醇-亚胺框架

初始缩合反应保留了醛单体的三个酚羟基:



画出一个中心苯环, 其上交替连接 OH 基团和  $-CH=N-$  支臂。氮原子通过对亚苯基连接体与相邻节点相连。

- 羟基化的三连接节点: Oc1c([\*:1])c(O)c([\*:2])c(O)c1[\*:3]
- 对亚苯基双亚胺连接体: [\*:1]/C=N/c1ccc(/N=C/[\*:2])cc1

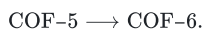
重复单元的化学式仍为  $C_{18}H_{12}N_3O_3$ 。

## COF-6: $\beta$ -酮烯胺框架

COF-5 发生质子转移和化学键重排:



这是互变异构化, 因此没有原子的增加或减少:



绘制重复单元时:

1. 将三个酚羟基  $\text{C}-\text{OH}$  基团替换为三个  $\text{C}=\text{O}$  基团。
2. 将每个环外  $-\text{CH}=\text{N}-\text{Ar}$  连接替换为  $=\text{CH}-\text{NH}-\text{Ar}$ 。
3. 将中心六元环的环原子之间均画为单键。

因此, 中心结构基元为 **2,4,6-三(芳氨基亚甲基)环己烷-1,3,5-三酮**:

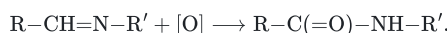
- **酮烯胺节点片段**: O=C1C(=CN[\*:1])C(=O)C(=CN[\*:2])C(=O)C1=CN[\*:3]
- **起连接作用的对亚苯基**: [\*:1]c1ccc([\*:2])cc1

重复单元仍为  $\text{C}_{18}\text{H}_{12}\text{N}_3\text{O}_3$ 。其中的氮原子现在是烯胺  $\text{NH}$  中的氮原子, 这解释了普通亚胺伸缩振动吸收带的缺失。

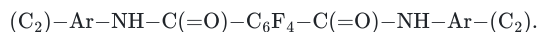
### 3.5 — 大环化合物 X 的最小重复单元

这里依次发生两步结构变化。

首先, COF-7 的亚胺被氧化为**酰胺**:

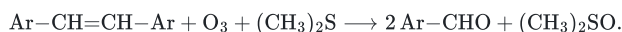


因此, 这些新生成的酰胺中, 每个羰基碳均来自 D4 的醛基, 每个酰胺氮均来自 C2。故正确的连接方向为



所用试剂为**亚氯酸钠**  $[\text{Na}^+].[ \text{O}- ]\text{Cl}=\text{O}$  和**磷酸二氢钠**  $[\text{Na}^+].[ \text{O}- ]\text{P}(=\text{O})(\text{O})\text{O}$ 。乙酸  $\text{CC}(=\text{O})\text{O}$  催化此前的亚胺形成反应。

其次, 还原性臭氧分解使 C2 中央的烯键断裂:



这里, 臭氧为  $[ \text{O}- ][ \text{O}^+ ]=\text{O}$ , 二甲硫醚为  $\text{csc}$ , 二甲基亚砷为  $\text{cs}(\text{c})=\text{O}$ 。

因此, C2 的每一半都变为一个 **3,5-双(4-氨基苯基)苯甲醛衍生片段**, 其中氨基已参与形成酰胺。对应的游离二胺为 **3,5-双(4-氨基苯基)苯甲醛**, O=Cc1cc(-c2ccc(N)cc2)cc(-c2ccc(N)cc2)c1。

X 的最小重复单元由以下部分组成:

- 一个中心苯环, 在交替位置上带有一个甲酰基和两个芳基取代基;
- 每条芳基支臂上的一个对亚苯基;
- 两处酰胺连接;
- 一个四氟取代苯环, 其上的两个羰基互为对位。

明确表示其重复片段的 SMILES 为

[\*:1]Nc1ccc(cc1)-c1cc(C=O)cc(c1)-c1ccc(cc1)NC(=O)c1c(F)c(F)c(c(F)c2F)C(=O)[\*:2]

将一个重复单元末端的羰基碳与下一个重复单元起始的氮相连。保留下来的六边形环路包含六个这样的重复单元, 形成**环状六聚体 X**,  $\text{C}_{162}\text{H}_{84}\text{F}_{24}\text{N}_{12}\text{O}_{18}$ 。其完整分子的 SMILES 为

N1c2ccc(cc2)-c2cc(C=O)cc(c2)-c2ccc(cc2)NC(=O)c2c(F)c(F)c(c(F)c2F)C(=O)Nc2ccc(cc2)-c2cc(C=O)cc(c2)-c2ccc(cc2)NC(=O)c2c(F)c(F)c(c(F)c2F)C(=O)Nc2ccc(cc2)-c2cc(C=O)cc(c2)-c2ccc(cc2)NC(=O)c2c(F)c(F)c(c(F)c2F)C(=O)Nc2ccc(cc2)-c2cc(C=O)cc(c2)-c2ccc(cc2)NC(=O)c2c(F)c(F)c(c(F)c2F)C(=O)Nc2ccc(cc2)-c2cc(C=O)cc(c2)-c2ccc(cc2)NC(=O)c2c(F)c(F)c(c(F)c2F)C(=O)1

这一表示指定了连接关系, 并不意味着该大环化合物具有唯一的三维构象。

### 3.6 — COF-8 的堆积能

一个原始重复单元包含一个 D2 衍生节点和一个 E1 衍生节点。其中的芳香环为:

- 来自 D2 的三个外围苯环;
- 来自 D2 的一个中心 1,3,5-三嗪环;
- 来自 E1 的一个苯环。

因此, 每个重复单元含有**四个苯环和一个三嗪环**。苯为 c1ccccc1; 1,3,5-三嗪为 c1ncncn1。

题给的 AA' 能量验证了这一计数:

$$4(-12.6) + (-16.7) = -67.1 \text{ kJ mol}^{-1}.$$

对于 AA, 所有对应的环均直接重叠:

$$E_{\text{AA}} = 4E_{\text{b-b}} + E_{\text{t-t}} = 4(-7.9) + (-6.7) = \boxed{-38.3 \text{ kJ mol}^{-1}}.$$

对于 AB, 位移使一个 E1 衍生的苯节点位于一个 D2 衍生的三嗪节点上方。每个原始重复单元有一处这样的芳香环接触。另一个节点位于孔的上方, 而外围亚苯基环之间并未相互对齐。

因此,

$$E_{AB} = E_{b-t} = \boxed{-49.8 \text{ kJ mol}^{-1}}.$$

对于略微错位的 **AB'** 排列，使用错位的苯-三嗪相互作用能：

$$E_{AB'} = \boxed{-55.6 \text{ kJ mol}^{-1}}.$$

接触对的计数如下：

| 排列           | b-b 对数 | b-t 对数 | t-t 对数 | 能量 / kJ mol <sup>-1</sup> |
|--------------|--------|--------|--------|---------------------------|
| AA           | 4      | 0      | 1      | -38.3                     |
| AA'，用于核对的题给值 | 4      | 0      | 1      | -67.1                     |
| AB           | 0      | 1      | 0      | -49.8                     |
| AB'          | 0      | 1      | 0      | -55.6                     |

尽管涉及两层，每对芳香环只计数一次。

### 3.7 — 吸附容量及每个孔中的铀酰离子数

吸附的铀酰离子质量为

$$\begin{aligned} m_{\text{absorbed}} &= (C_0 - C_e)V \\ &= (19.90 - 9.225) \text{ mg dm}^{-3} \times 0.2000 \text{ dm}^3 \\ &= 2.135 \text{ mg}. \end{aligned}$$

因此

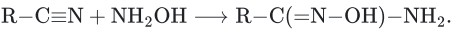
$$q_e = \frac{2.135 \text{ mg}}{0.005000 \text{ g}} = \boxed{427.0 \text{ mg g}^{-1}}.$$

为确定每个孔中的离子数，首先求出一个孔所对应的框架质量。

D2 和 E1 的分子式分别为 C<sub>24</sub>H<sub>15</sub>N<sub>3</sub>O<sub>3</sub> 和 C<sub>12</sub>H<sub>9</sub>N<sub>3</sub>。每个重复单元发生三次缩合，得到



羟胺 NO 将每个腈基转化为**偕胺肟基团**，可表示为 [\*]C(=NO)N：



每个重复单元有三个腈基，因此



于是，

$$\begin{aligned} M_{\text{COF-9,repeat}} &= 36(12.01) + 27(1.008) + 9(14.01) + 3(16.00) \\ &= 633.666 \text{ g mol}^{-1}. \end{aligned}$$

一个蜂窝孔有六个顶点，每个顶点由三个孔共享。因此，一个孔对应两个完整节点：一个 D2 衍生节点和一个 E1 衍生节点。所以，一个原始重复单元对应一个孔。

铀酰离子 O=[U+2]=O 具有线形 O-U-O 单元，其摩尔质量为

$$M_{\text{UO}_2^{2+}} = 238.03 + 2(16.00) = 270.03 \text{ g mol}^{-1}.$$

实验中的物质的量为

$$\begin{aligned} n_{\text{UO}_2^{2+}} &= \frac{2.135 \times 10^{-3}}{270.03} = 7.907 \times 10^{-6} \text{ mol}, \\ n_{\text{pores}} &= \frac{5.000 \times 10^{-3}}{633.666} = 7.891 \times 10^{-6} \text{ mol}. \end{aligned}$$

二者之比为

$$\frac{n_{\text{UO}_2^{2+}}}{n_{\text{pores}}} = 1.002 \approx \boxed{1 \text{ 个铀酰离子/孔}}.$$

解答已与官方解答核对。

## 题目 4：乌兹别克斯坦的核历史

### T4. 乌兹别克斯坦的核历史

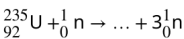
6%

| 4.1 | 4.2 | 4.3 | 4.4 | 4.5 | 4.6 | 4.7 | 4.8 | 4.9 | Σ  |
|-----|-----|-----|-----|-----|-----|-----|-----|-----|----|
| 2   | 3   | 3   | 2   | 2   | 2   | 2   | 2   | 4   | 22 |

天然铀主要由两种同位素组成，即 <sup>235</sup>U 和 <sup>238</sup>U。<sup>235</sup>U 是维持核裂变反应的同位素。

**4.1** 假设天然铀仅由同位素 <sup>235</sup>U (235.04 a.u.) 和 <sup>238</sup>U (238.05 a.u.) 组成，计算天然铀中 <sup>235</sup>U 的原子丰度。**2.0** 分

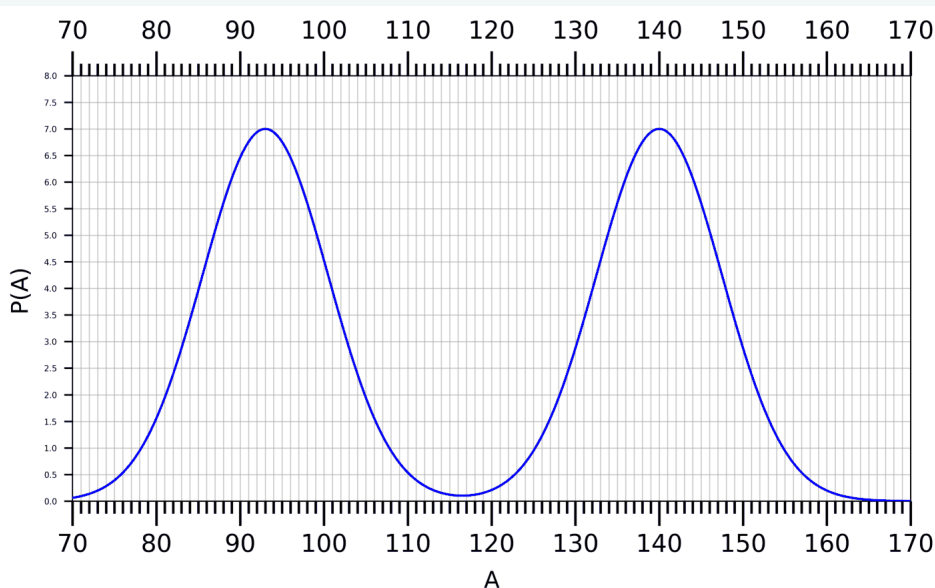
核电站中发生的主要反应是 <sup>235</sup>U 吸收一个中子后发生裂变，释放能量并产生三个额外的中子，从而维持链式反应。



引发链式反应的中子可通过以下几种方式产生：

- a) 反应堆堆芯内  $^{11}\text{B}$  与  $\alpha$  粒子的反应
- b)  $\gamma$  射线与反应堆冷却水中存在的  $^2\text{D}$  原子核的相互作用
- c)  $^9\text{Be}$  与外部安装的中子源中产生的  $\alpha$  粒子的反应。

4.2 写出 (a)、(b) 和 (c) 的核反应方程式。3.0 分



上图显示了  $^{235}\text{U}$  裂变产物的百分产额  $P(A)$  随质量数  $A$  的分布。

4.3 写出  $^{235}\text{U}$  吸收中子后发生裂变的主要核裂变方程式。该反应生成的两种元素位于元素周期表的同一族。3.0 分

4.4 若结合能  $BE(^{235}\text{U}) = 7.59 \text{ MeV/nucleon}$ ，且裂变产物的平均结合能为  $BE(\text{裂变产物}) = 8.45 \text{ MeV/nucleon}$ ，计算该反应释放的能量 ( $\Delta E$ , MeV)。忽略自由中子的结合能。2.0 分

裂变中子产生时的平均能量为  $2 \text{ MeV}$ ，并通过与原子核的多次散射而减速。经过若干次碰撞后，中子的速度降低，直至其平均动能与周围原子或分子的平均动能相同。

对数能降  $\xi$  表示每次碰撞中，中子能量的对数的平均减少量：

$$\xi = \ln \left( \frac{E_{\text{initial}}}{E_{\text{final}}} \right)$$

$E_{\text{initial}}$  和  $E_{\text{final}}$  分别为每次碰撞前、后的中子能量。

对于每种材料， $\xi$  均为常数，与中子的初始能量无关。

4.5 以水为慢化剂，确定将中子从  $2 \text{ MeV}$  慢化至  $0.012 \text{ eV}$  所需的平均碰撞次数  $n_c$ 。 $\xi(\text{水}) = 0.948$  2.0 分

1963 年，乌尔塔布拉克气田发生了失控的天然气井喷，大量甲烷喷出并燃烧。

4.6 计算在  $298 \text{ K}$  下每摩尔甲烷燃烧反应的  $\Delta_r H_{298}^\circ$  ( $\text{kJ mol}^{-1}$ )。假设所有物质均为气态。使用下列热力学数据。2.0 分

|                                                         |                                        |
|---------------------------------------------------------|----------------------------------------|
| $\Delta_f H_{298}^\circ(\text{CH}_4)$                   | $-74.8 \text{ kJ mol}^{-1}$            |
| $\Delta_f H_{298}^\circ(\text{H}_2\text{O}, \text{气态})$ | $-241.8 \text{ kJ mol}^{-1}$           |
| $\Delta_f H_{298}^\circ(\text{CO}_2)$                   | $-393.5 \text{ kJ mol}^{-1}$           |
| $C_P(\text{CH}_4)$                                      | $35 \text{ J mol}^{-1} \text{ K}^{-1}$ |
| $C_P(\text{H}_2\text{O}, \text{气态})$                    | $34 \text{ J mol}^{-1} \text{ K}^{-1}$ |
| $C_P(\text{O}_2)$                                       | $29 \text{ J mol}^{-1} \text{ K}^{-1}$ |
| $C_P(\text{CO}_2)$                                      | $37 \text{ J mol}^{-1} \text{ K}^{-1}$ |

若未能求得 4.6 的答案，请在后续计算中使用  $\Delta_r H_{298}^\circ = -750 \text{ kJ mol}^{-1}$ 。

4.7 计算在  $2000 \text{ K}$  下每摩尔甲烷燃烧反应的  $\Delta_r H_{2000}$  ( $\text{kJ mol}^{-1}$ )。假设所有物质均为气态。2.0 分

若未能求得 4.7 的答案，请在后续计算中使用  $\Delta_r H_{2000} = -700 \text{ kJ mol}^{-1}$ 。

假设甲烷在着火前以  $101.325 \text{ kPa}$ 、 $298 \text{ K}$  的状态从井中流出，体积流量为每天  $Q = 2.2 \times 10^5 \text{ m}^3$ 。

4.8 计算甲烷在  $T = 2000 \text{ K}$  下完全等温燃烧时每天释放的总能量  $E$  (单位为  $\text{J day}^{-1}$ )。2.0 分

通过引爆一次 TNT 当量为 30 千吨的地下核爆炸，使储气层坍塌并封堵泄漏，乌尔塔布拉克气田的天然气泄漏得以终止。1 吨 TNT 当量对应  $4.184 \text{ GJ}$  的能量。

4.9 使用 4.4 中的数值，计算核爆炸期间的裂变总次数  $TN$ 。假设所用浓缩铀中  $^{235}\text{U}$  同位素的质量分数为 90%，且其中 33% 的  $^{235}\text{U}$  发生了裂变，计算爆炸中所用浓缩铀的质量  $m$  (单位为  $\text{kg}$ )。

若未能求得 4.4 的答案，请使用  $\Delta E = 200 \text{ MeV}$ 。4.0 分

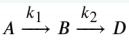
物理常数与方程

常数

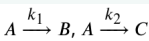
|              |                                                  |
|--------------|--------------------------------------------------|
| 阿伏伽德罗常数      | $N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$    |
| 摩尔气体常数       | $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$    |
| 法拉第常数        | $F = 96485 \text{ C mol}^{-1}$                   |
| 普朗克常数        | $h = 6.626 \times 10^{-34} \text{ J s}$          |
| 真空中的光速       | $c = 2.998 \times 10^8 \text{ m s}^{-1}$         |
| 电子质量         | $m_e = 9.109 \times 10^{-31} \text{ kg}$         |
| 电子电荷量        | $e = 1.602 \times 10^{-19} \text{ C}$            |
| 标准压力         | $P^\circ = 1 \text{ bar} = 10^5 \text{ Pa}$      |
| 25 °C 时水的离子积 | $K_w = 1.00 \times 10^{-14}$                     |
| 摄氏温标的零点      | $0^\circ\text{C} = 273.15 \text{ K}$             |
| 电子伏特         | $1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}$ |
| 瓦特           | $1 \text{ W} = 1 \text{ J s}^{-1}$               |
| 库仑           | $1 \text{ C} = 1 \text{ A s}$                    |
| 纳米           | $1 \text{ nm} = 1 \times 10^{-9} \text{ m}$      |
| 埃            | $1 \text{ \AA} = 1 \times 10^{-10} \text{ m}$    |
| 公吨           | $1 \text{ ton} = 1000 \text{ kg}$                |
| 升            | $1 \text{ L} = 1 \text{ dm}^3$                   |

方程

|                                              |                                                                            |
|----------------------------------------------|----------------------------------------------------------------------------|
| 理想气体状态方程                                     | $PV = nRT$                                                                 |
| 道尔顿定律                                        | $P_i = x_i P$                                                              |
| 朗伯-比尔定律                                      | $A = \log_{10} \frac{I_0}{I} = \varepsilon cl$                             |
| 光子的能量                                        | $E = h\nu = \frac{hc}{\lambda}$                                            |
| 热量与温度变化                                      | $Q = nC_m \Delta T$                                                        |
| 吉布斯能的定义                                      | $G = H - TS$                                                               |
| 吉布斯能与平衡常数                                    | $\Delta_r G^\circ = -RT \ln K$                                             |
| 焓变与温度的关系 (当 $\Delta_r C_p = \text{const}$ 时) | $\Delta_r H_{T_2} = \Delta_r H_{T_1} + \Delta_r C_p (T_2 - T_1)$           |
| 熵变与温度的关系 (当 $\Delta_r C_p = \text{const}$ 时) | $\Delta_r S_{T_2} = \Delta_r S_{T_1} + \Delta_r C_p \ln \frac{T_2}{T_1}$   |
| 亨德森-哈塞尔巴尔赫方程                                 | $\text{pH} = \text{p}K_a + \log_{10} \frac{[\text{A}^-]}{[\text{HA}]}$     |
| 平均反应速率                                       | $r = \frac{\Delta c}{\Delta t}$                                            |
| 速率方程                                         | $r = k[\text{A}]^x [\text{B}]^y$                                           |
| 阿伦尼乌斯方程                                      | $k = A \exp \left( -\frac{E_a}{RT} \right)$                                |
| 一级反应的积分速率方程                                  | $c = c_0 e^{-kt}$<br>$kt = \ln \frac{c_0}{c}$                              |
| 一级反应中反应物的寿命                                  | $\tau = \frac{1}{k}$                                                       |
| n 级反应的积分速率方程 ( $n \neq 1$ )                  | $kt = \frac{1}{n-1} (c^{1-n} - c_0^{1-n})$ , 其中 $n \neq 1$                 |
| 连续反应中中间体的浓度:                                 | $[\text{B}] = \frac{k_1[\text{A}]_0}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t})$ |



|             |                                                   |
|-------------|---------------------------------------------------|
| 竞争反应中的产物比例: | $\frac{[\text{B}]}{[\text{C}]} = \frac{k_1}{k_2}$ |
|-------------|---------------------------------------------------|



|              |                                                          |
|--------------|----------------------------------------------------------|
| 米氏方程         | $r_0 = r_{\max} \frac{[\text{S}]_0}{K_M + [\text{S}]_0}$ |
| 比表面积         | $s = \frac{S}{m}$                                        |
| 数列：等差数列、等比数列 | $a_n = a_1 + d(n-1)$<br>$a_n = a_1 q^{n-1}$              |
| 等比数列求和       | $\sum_{k=0}^n a_1 q^k = a_1 \frac{q^{n+1} - 1}{q - 1}$   |

|                           |                            |
|---------------------------|----------------------------|
| 半径为 $r$ 的球的体积             | $V = \frac{4}{3}\pi r^3$   |
| 半径为 $r$ 的球的表面积            | $S = 4\pi r^2$             |
| 底面半径为 $r$ 、高为 $h$ 的圆锥体的体积 | $V = \frac{1}{3}\pi r^2 h$ |
| 底面半径为 $r$ 、高为 $h$ 的圆柱体的体积 | $V = \pi r^2 h$            |

将所有气体视为理想气体。

在平衡常数的计算中，所有浓度均以  $1 \text{ mol dm}^{-3}$  的浓度为参照。

#### 元素周期表

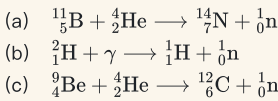
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| 19<br>K<br>39.10  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  | 20<br>Ca<br>40.08 |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  | 21<br>Sc<br>44.96 |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  | 22<br>Ti<br>47.87 |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  | 23<br>V<br>50.94  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  | 24<br>Cr<br>52.00 |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  | 25<br>Mn<br>54.94 |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  | 26<br>Fe<br>55.85 |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  | 27<br>Co<br>58.93 |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  | 28<br>Ni<br>58.69 |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  | 29<br>Cu<br>63.55 |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  | 30<br>Zn<br>65.38 |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  | 31<br>Ga<br>69.72 |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  | 32<br>Ge<br>72.63 |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  | 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| 37<br>Rb<br>85.47 |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  | 38<br>Sr<br>87.62 |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  | 39<br>Y<br>88.91  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  | 40<br>Zr<br>91.22 |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  | 41<br>Nb<br>92.91 |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  | 42<br>Mo<br>95.95 |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  | 43<br>Tc<br>-     |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  | 44<br>Ru<br>101.1 |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  | 45<br>Rh<br>102.9 |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  | 46<br>Pd<br>106.4 |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  | 47<br>Ag<br>107.9 |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  | 48<br>Cd<br>112.4 |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  | 49<br>In<br>114.8 |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  | 50<br>Sn<br>118.7 |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  | 51<br>Sb<br>121.8 |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  | 52<br>Te<br>127.6 |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  | 53<br>I<br>126.9  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  | 54<br>Xe<br>131.3 |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  | 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| 55<br>Cs<br>132.9 |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  | 56<br>Ba<br>137.3 |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  | 57-71             |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  | 72<br>Hf<br>178.5 |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  | 73<br>Ta<br>180.9 |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  | 74<br>W<br>183.8  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  | 75<br>Re<br>186.2 |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  | 76<br>Os<br>190.2 |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  | 77<br>Ir<br>192.2 |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  | 78<br>Pt<br>195.1 |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  | 79<br>Au<br>197.0 |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  | 80<br>Hg<br>200.6 |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  | 81<br>Tl<br>204.4 |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  | 82<br>Pb<br>207.2 |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  | 83<br>Bi<br>209.0 |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  | 84<br>Po<br>-     |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  | 85<br>At<br>-     |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  | 86<br>Rn<br>-     |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  | 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115<br>Mc<br>-    |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  | 116<br>Lv<br>-    |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  | 117<br>Ts<br>-    |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  | 118<br>Og<br>-    |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  | 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题目译自官方英文原文。

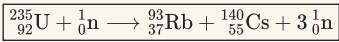
#### 答案

- 4.1:  $^{235}\text{U}$  的原子丰度为  $0.664\% \approx 0.66\%$ 。

- 4.2:



- 4.3: 裂变碎片为铷-93 和铯-140，两者均为第 1 族元素：



- 4.4: 每次裂变释放  $\Delta E = 185.2 \text{ MeV}$ 。

- 4.5:  $n_c = 19.97 \approx 20$  次碰撞。

- 4.6:  $\Delta_r H_{298}^\circ = -802.3 \text{ kJ mol}^{-1}$ 。

- 4.7:  $\Delta_r H_{2000} = -781.9 \text{ kJ mol}^{-1}$ 。

- 4.8:  $E \approx 7.0 \times 10^{12} \text{ J day}^{-1}$ 。

- 4.9:  $TN \approx 4.23 \times 10^{24}$  次裂变；浓缩铀的质量为  $m \approx 5.6 \text{ kg}$ 。

#### 解答

##### 4.1 — 原子丰度

题目所附元素周期表给出的天然铀平均原子质量为  $238.03 \text{ a.u.}$ 。设  $^{235}\text{U}$  的原子分数为  $x$ ，则  $^{238}\text{U}$  的原子分数为  $1 - x$ ，因此

$$238.03 = 235.04x + 238.05(1 - x).$$

所以,

$$x = \frac{238.05 - 238.03}{238.05 - 235.04} = \frac{0.02}{3.01} = 0.0066445.$$

因此, 使用题目给出的经舍入的原子质量, 可得

$$100x = 0.66445\% \approx 0.66\%.$$

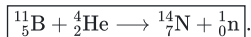
#### 4.2 — 产生中子的反应

在每个核反应中, 质量数  $A$  和原子序数  $Z$  均守恒。 $\alpha$  粒子是氦-4 原子核, 即  ${}^4_2\text{He}$ 。

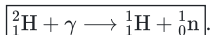
(a) 发射一个中子后, 剩余原子核的质量数和原子序数为

$$A = 11 + 4 - 1 = 14, \quad Z = 5 + 2 = 7.$$

原子序数为 7 的元素是氮, 因此产物为氮-14:



(b) 氘核  ${}^2_1\text{H}$  含有一个质子和一个中子。吸收能量足够高的光子后, 两者分离:

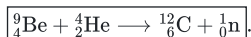


氢-1 原子核就是质子。

(c) 剩余原子核的质量数和原子序数为

$$A = 9 + 4 - 1 = 12, \quad Z = 4 + 2 = 6.$$

原子序数为 6 的元素是碳, 因此生成碳-12:



这些核反应方程式表示的是原子核; 电子数不参与配平。

#### 4.3 — 裂变碎片的确定

题目所给图中的两个峰值大致位于

$$A_{\text{轻}} = 93, \quad A_{\text{重}} = 140.$$

两者之和为 233, 与题目所述发射三个中子相符:

$$235 + 1 = 93 + 140 + 3.$$

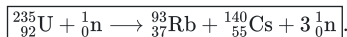
原子序数守恒要求

$$Z_{\text{轻}} + Z_{\text{重}} = 92.$$

铷和铯满足同族条件: 两者均为第 1 族元素, 且

$$Z(\text{Rb}) + Z(\text{Cs}) = 37 + 55 = 92.$$

将铷指定为较轻的碎片、铯指定为较重的碎片, 得到



质量数和原子序数均已配平。

#### 4.4 — 每次裂变释放的能量

释放的能量等于总核结合能的增加量。

初始时, 铀核含有 235 个束缚核子。入射中子是自由中子, 在题目给定的近似下不贡献结合能。最终, 两个碎片共含有

$$93 + 140 = 233$$

个束缚核子; 发射出的三个中子均为自由中子。

因此,

$$\begin{aligned} \Delta E &= BE_{\text{产物}} - BE_{\text{反应物}} \\ &= 233(8.45) - 235(7.59) \\ &= 1968.85 - 1783.65 \\ &= \boxed{185.2 \text{ MeV}}. \end{aligned}$$

这一正值为每次裂变释放的能量。

#### 4.5 — 平均碰撞次数

慢化剂为水,  $\text{H}_2\text{O}$ , SMILES 为 o。

由于连续碰撞中的对数能降可以相加,

$$\ln\left(\frac{E_0}{E_f}\right) = n_c \xi.$$

分子和分母使用相同的能量单位,

$$E_0 = 2 \text{ MeV} = 2 \times 10^6 \text{ eV}.$$

因此,

$$n_c = \frac{\ln\left(\frac{2 \times 10^6}{0.012}\right)}{0.948} = 19.9699.$$

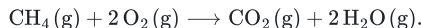
所以,

$$n_c \approx 20 \text{ 次碰撞}.$$

#### 4.6 — 298 K 下的甲烷燃烧

涉及的分子为甲烷,  $\text{CH}_4$ , SMILES 为  $\text{C}$ ; 氧气,  $\text{O}_2$ , SMILES 为  $\text{O}=\text{O}$ ; 二氧化碳,  $\text{CO}_2$ , SMILES 为  $\text{O}=\text{C}=\text{O}$ ; 以及水,  $\text{H}_2\text{O}$ , SMILES 为  $\text{O}$ .

一摩尔甲烷完全燃烧的反应为



根据盖斯定律,

$$\Delta_r H_{298}^\circ = \sum_{\text{产物}} \nu_i \Delta_f H_i^\circ - \sum_{\text{反应物}} \nu_i \Delta_f H_i^\circ.$$

$\text{O}_2(\text{g})$  是处于参考状态的单质, 其标准生成焓为零。因此

$$\begin{aligned} \Delta_r H_{298}^\circ &= [-393.5 + 2(-241.8)] - [-74.8 + 2(0)] \\ &= \boxed{-802.3 \text{ kJ mol}^{-1}}. \end{aligned}$$

负号表示该反应为放热反应。

#### 4.7 — 2000 K 下的甲烷燃烧

对于同一配平后的燃烧反应,

$$\begin{aligned} \Delta_r C_P &= C_P(\text{CO}_2) + 2C_P(\text{H}_2\text{O}) - C_P(\text{CH}_4) - 2C_P(\text{O}_2) \\ &= 37 + 2(34) - 35 - 2(29) \\ &= 12 \text{ J mol}^{-1} \text{ K}^{-1} \\ &= 0.012 \text{ kJ mol}^{-1} \text{ K}^{-1}. \end{aligned}$$

将题目给出的热容视为常数, 根据基尔霍夫定律可得

$$\begin{aligned} \Delta_r H_{2000} &= \Delta_r H_{298}^\circ + \Delta_r C_P(2000 - 298) \\ &= -802.3 + 0.012(1702) \\ &= -781.876 \text{ kJ mol}^{-1}. \end{aligned}$$

所以,

$$\boxed{\Delta_r H_{2000} \approx -781.9 \text{ kJ mol}^{-1}}.$$

#### 4.8 — 每天释放的能量

体积流量是在 298 K 下给出的, 因此将气体体积换算为甲烷的物质的量时, 必须使用该温度。

由理想气体状态方程, 摩尔流量为

$$\begin{aligned} \dot{n} &= \frac{pQ}{RT} \\ &= \frac{(101325 \text{ Pa})(2.2 \times 10^5 \text{ m}^3 \text{ day}^{-1})}{(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(298 \text{ K})} \\ &= 8.9973 \times 10^6 \text{ mol day}^{-1}. \end{aligned}$$

这里,  $\text{Pa m}^3 = \text{J}$ 。释放的能量为燃烧焓的绝对值, 是一个正值:

$$\begin{aligned} E &= -\dot{n} \Delta_r H_{2000} \\ &= (8.9973 \times 10^6 \text{ mol day}^{-1})(781876 \text{ J mol}^{-1}) \\ &= 7.0348 \times 10^{12} \text{ J day}^{-1}. \end{aligned}$$

保留两位有效数字, 与体积流量的精度一致, 得

$$\boxed{E = 7.0 \times 10^{12} \text{ J day}^{-1}}.$$

#### 4.9 — 裂变次数与铀的质量

30 千吨 TNT 所对应的总能量为

$$\begin{aligned} E_{\text{爆炸}} &= (30 \times 10^3 \text{ ton})(4.184 \times 10^9 \text{ J ton}^{-1}) \\ &= 1.2552 \times 10^{14} \text{ J}. \end{aligned}$$

利用 4.4 的结果, 以焦耳表示的每次裂变释放的能量为

$$\begin{aligned} \varepsilon_{\text{裂变}} &= (185.2 \text{ MeV})(10^6 \text{ eV MeV}^{-1})(1.602 \times 10^{-19} \text{ J eV}^{-1}) \\ &= 2.966904 \times 10^{-11} \text{ J}. \end{aligned}$$

因此, 裂变总次数为

$$TN = \frac{E_{\text{爆炸}}}{\varepsilon_{\text{裂变}}} = \frac{1.2552 \times 10^{14}}{2.966904 \times 10^{-11}} = \boxed{4.23 \times 10^{24} \text{ 次裂变}}.$$

每次裂变消耗一个  $^{235}\text{U}$  原子核。因此, 实际发生裂变的  $^{235}\text{U}$  的质量为

$$\begin{aligned} m_{\text{已裂变}} &= \frac{TN}{N_A} M(^{235}\text{U}) \\ &= \frac{4.23067 \times 10^{24}}{6.022 \times 10^{23} \text{ mol}^{-1}} (235.04 \text{ g mol}^{-1}) \\ &= 1651.24 \text{ g} = 1.65124 \text{ kg}. \end{aligned}$$

若  $m$  为浓缩铀的初始质量，则其中  $^{235}\text{U}$  的初始质量为  $0.90m$ 。由于该同位素中有 33% 发生了裂变，

$$m_{\text{已裂变}} = 0.33(0.90m).$$

因此

$$m = \frac{1.65124}{0.33 \times 0.90} = 5.5597 \text{ kg}.$$

适当舍入后，

$$m \approx 5.6 \text{ kg}.$$

解答已与官方解答核对。

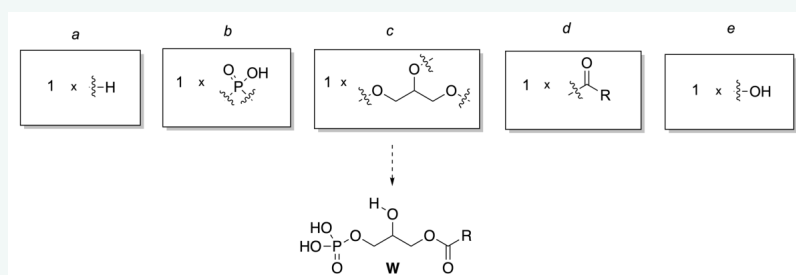
## 题目 5：心磷脂

### T5. 心磷脂

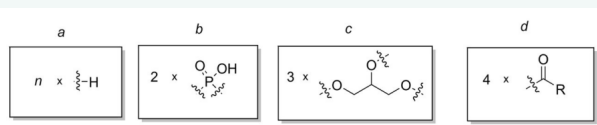
6%

| 5.1 | 5.2 | 5.3 | 5.4 | 5.5 | 5.6 | $\Sigma$ |
|-----|-----|-----|-----|-----|-----|----------|
| 1   | 6   | 4   | 2   | 2   | 3   | 18       |

本题要求你发挥创造力，用片段构建分子。例如，若要求你用片段  $a-e$  画一种手性磷脂，如 **W**，则可按下图所示进行组装。



心磷脂是一类脂肪酸残基各不相同的无环磷脂。它们对能量生成和膜的稳定性至关重要。心磷脂的缺陷可导致某些疾病。**PL1** 属于这一类。仅使用下列指定数量的结构单元  $a-d$ ，即可组装出 **PL1** 的未电离形式。 $R$  是脂肪酸结构中的烃基取代基。



**PL1** 不含任何过氧键。

**5.1 勾选关于  $n$  ( $a$  型片段的数量) 取值的一项正确陈述。1.0 分**

- (a)  $n$  是偶数，  
 (b)  $n$  是奇数，  
 (c)  $n$  既可以是奇数，也可以是偶数。

有些心磷脂即使含有四个相同的脂肪酸残基，仍是手性分子，**PL1** 就是如此。**PL1** 的一个对映异构体存在于原核生物和真核生物中，另一个则仅存在于古菌中。**PL1** 的所有其他非对映异构体均为非手性分子，因为它们具有对称面。不考虑磷原子作为立体中心所产生的手性。

**PL1** 是一种具有相同酸性基团的二元酸。由于单阴离子 **Y** 具有特殊的稳定结构，其第二次去质子化较难发生 ( $pK_{a_2} \gg pK_{a_1}$ )。

**5.2 画出 **PL1** 的一个对映异构体的结构。画出 **Y** 的结构，并在图中体现能够解释  $pK_{a_1}$  与  $pK_{a_2}$  差异的稳定作用。用缩写  $R$  表示脂肪酸残基。6.0 分**  
 为鉴定主要存在于哺乳动物心脏中的 **PL1** 所含的脂肪酸 ( $\text{RCOOH}$ )，进行了一系列实验。在还原性臭氧分解过程中， $\text{RCOOH}$  生成三种不同的有机产物，且它们的物质的量相等。

**5.3 确定该脂肪酸 ( $\text{RCOOH}$ ) 的分子式，已知 **PL1** 的未电离形式中原子间的  $\sigma$  键和  $\pi$  键总数为 255。用计算支持你的答案。4.0 分**

如果你未能确定 **PL1** 的结构式，可以使用 5.1 中的  $a-d$  片段。

100 g  $\text{RCOOH}$  与 181.0 g 碘反应。 $\text{RCOOH}$  也以类似方式与 **X** 反应，形成碘的质量分数为 36.57% 的加成产物。

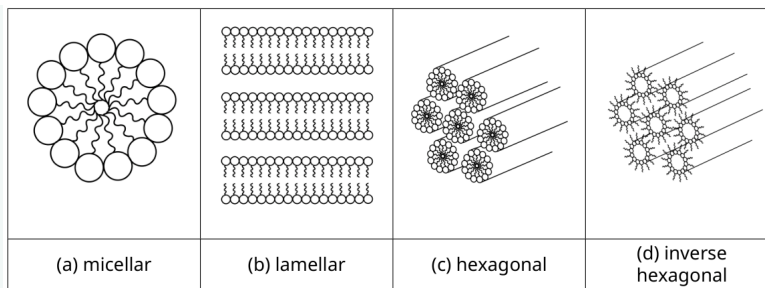
**5.4 确定 **X** 的分子式。用计算支持你的答案。2.0 分**

**PL1** 的相行为取决于 pH。在生理条件下，**PL1** 为二价阴离子，并形成层状相。

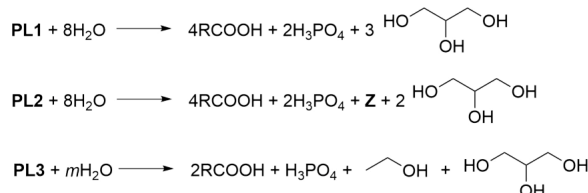
**5.5 当 **PL1** 中的两个酸性残基均被质子化时，它会形成哪种脂质相？2.0 分**

注意，解答本题不需要知道 **PL1** 的结构。

勾选正确答案。



下列已配平的反应方程式表示磷脂 PL1–PL3 的水解：



- PL2 的末电离形式中原子间的  $\sigma$  键和  $\pi$  键总数为 254。它是一个手性分子，且对称性比 PL1 更高，
- Z 仅含 C、H 和 O，且在催化剂存在下不与  $\text{H}_2$  反应，
- 磷脂 PL3 在生理 pH 下是带电分子，并以一对对映异构体的形式存在。

5.6 画出 PL2 和 PL3 的结构，用 R 表示脂肪酸残基。在适当的位置标明立体化学。3.0 分

元素周期表

|                   |                   |                      |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   |
|-------------------|-------------------|----------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|
| 1<br>H<br>1.008   |                   |                      |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   | 18<br>He<br>4.003 |
| 3<br>Li<br>6.94   | 4<br>Be<br>9.01   |                      |                   |                   |                   |                   |                   |                   |                   |                   |                   | 5<br>B<br>10.81   | 6<br>C<br>12.01   | 7<br>N<br>14.01   | 8<br>O<br>16.00   | 9<br>F<br>19.00   | 10<br>Ne<br>20.18 |
| 11<br>Na<br>22.99 | 12<br>Mg<br>24.30 | 13<br>Al<br>26.98    | 14<br>Si<br>28.09 | 15<br>P<br>30.97  | 16<br>S<br>32.06  | 17<br>Cl<br>35.45 | 18<br>Ar<br>39.95 |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   |
| 19<br>K<br>39.10  | 20<br>Ca<br>40.08 | 21<br>Sc<br>44.96    | 22<br>Ti<br>47.87 | 23<br>V<br>50.94  | 24<br>Cr<br>52.00 | 25<br>Mn<br>54.94 | 26<br>Fe<br>55.85 | 27<br>Co<br>58.93 | 28<br>Ni<br>58.69 | 29<br>Cu<br>63.55 | 30<br>Zn<br>65.38 | 31<br>Ga<br>69.72 | 32<br>Ge<br>72.63 | 33<br>As<br>74.92 | 34<br>Se<br>78.97 | 35<br>Br<br>79.90 | 36<br>Kr<br>83.80 |
| 37<br>Rb<br>85.47 | 38<br>Sr<br>87.62 | 39<br>Y<br>88.91     | 40<br>Zr<br>91.22 | 41<br>Nb<br>92.91 | 42<br>Mo<br>95.95 | 43<br>Tc<br>-     | 44<br>Ru<br>101.1 | 45<br>Rh<br>102.9 | 46<br>Pd<br>106.4 | 47<br>Ag<br>107.9 | 48<br>Cd<br>112.4 | 49<br>In<br>114.8 | 50<br>Sn<br>118.7 | 51<br>Sb<br>121.8 | 52<br>Te<br>127.6 | 53<br>I<br>126.9  | 54<br>Xe<br>131.3 |
| 55<br>Cs<br>132.9 | 56<br>Ba<br>137.3 | 57-71<br>La<br>138.9 | 72<br>Hf<br>178.5 | 73<br>Ta<br>180.9 | 74<br>W<br>183.8  | 75<br>Re<br>186.2 | 76<br>Os<br>190.2 | 77<br>Ir<br>192.2 | 78<br>Pt<br>195.1 | 79<br>Au<br>197.0 | 80<br>Hg<br>200.6 | 81<br>Tl<br>204.4 | 82<br>Pb<br>207.2 | 83<br>Bi<br>209.0 | 84<br>Po<br>-     | 85<br>At<br>-     | 86<br>Rn<br>-     |
| 87<br>Fr<br>-     | 88<br>Ra<br>-     | 89-103<br>Ac<br>-    | 104<br>Rf<br>-    | 105<br>Db<br>-    | 106<br>Sg<br>-    | 107<br>Bh<br>-    | 108<br>Hs<br>-    | 109<br>Mt<br>-    | 110<br>Ds<br>-    | 111<br>Rg<br>-    | 112<br>Cn<br>-    | 113<br>Nh<br>-    | 114<br>Fl<br>-    | 115<br>Mc<br>-    | 116<br>Lv<br>-    | 117<br>Ts<br>-    | 118<br>Og<br>-    |
|                   |                   |                      |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   |
| 57<br>La<br>138.9 | 58<br>Ce<br>140.1 | 59<br>Pr<br>140.9    | 60<br>Nd<br>144.2 | 61<br>Pm<br>-     | 62<br>Sm<br>150.4 | 63<br>Eu<br>152.0 | 64<br>Gd<br>157.3 | 65<br>Tb<br>158.9 | 66<br>Dy<br>162.5 | 67<br>Ho<br>164.9 | 68<br>Er<br>167.3 | 69<br>Tm<br>168.9 | 70<br>Yb<br>173.0 | 71<br>Lu<br>175.0 |                   |                   |                   |
| 89<br>Ac<br>-     | 90<br>Th<br>232.0 | 91<br>Pa<br>231.0    | 92<br>U<br>238.03 | 93<br>Np<br>-     | 94<br>Pu<br>-     | 95<br>Am<br>-     | 96<br>Cm<br>-     | 97<br>Bk<br>-     | 98<br>Cf<br>-     | 99<br>Es<br>-     | 100<br>Fm<br>-    | 101<br>Md<br>-    | 102<br>No<br>-    | 103<br>Lr<br>-    |                   |                   |                   |

题目译自官方英文原文。

## 答案

在下列通用结构的 SMILES 中，每个 \* 均表示相同的烃基取代基 R。按题目要求省略磷的立体化学。

- 5.1: (b),  $n$  是奇数。具体而言,  $n = 1$ 。
- 5.2: PL1 是心磷脂, 即 1,3-双(磷脂酰)甘油。其中一个对映异构体的两个外侧甘油立体中心均为  $S$ , 其结构为  
\*C(=O)OC[C@H](OC(=O)\*)COP(=O)(O)OCC(O)COP(=O)(O)OC[C@H](OC(=O)\*)COC(=O)\*

Y 是心磷脂单阴离子。一种质子定域的表达形式为

\*C(=O)OC[C@H](OC(=O)\*)COP(=O)(O)OC[C@H](O)COP(=O)([O-])OC[C@H](OC(=O)\*)COC(=O)\*

画出两个分子内氢键：磷酸基团的 O–H 向中央甘油的氧原子提供氢键，而该氧原子上的 O–H 向另一个磷酸基团中带负电的氧原子提供氢键。

- 5.3:  $\text{C}_{18}\text{H}_{32}\text{O}_2$ , 一种十八碳二烯酸。一个符合条件的代表是亚油酸, 即 (9Z, 12Z)-十八碳-9,12-二烯酸:  
CCCCC/C=C\C/C=C\CCCCCCCC(=O)O  
所给数据不能唯一确定双键的位置或几何构型。
- 5.4:  $\text{IBr}$ , 一溴化碘,  $\text{IBr}$ 。
- 5.5: (d), 反六方相。
- 5.6: PL2 是 2'-脱氧心磷脂, 含有一个丙烷-1,3-二醇桥连单元。其一个对映异构体为  
\*C(=O)OC[C@H](OC(=O)\*)COP(=O)(O)OCCOP(=O)(O)OC[C@@H](OC(=O)\*)COC(=O)\*

Z 是丙烷-1,3-二醇,  $\text{OCCCO}$ 。

PL3 是磷脂酰乙醇。其在生理条件下形成的单离子的一个对映异构体为  
CCOP(=O)([O-])OC[C@H](OC(=O)\*)COC(=O)\*

其另一个对映异构体将  $@$  替换为  $@$ 。水解反应的系数为  $m = 4$ 。

## 解答

### 5.1 一 氢片段的数量

每个甘油片段有三个连接位点, 每个磷片段有两个, 每个酰基片段有一个。因此, 计入氢片段后, 连接位点的数量为

$$3(3) + 2(2) + 4(1) + n = 17 + n.$$

每形成一个新键都会消耗两个连接位点, 因此  $17 + n$  必须为偶数。所以,  $n$  是奇数, 答案为 (b)。

由无环性可求出其确切值。共有  $9 + n$  个片段, 将它们连接成一个无环分子需要  $8 + n$  个片段间的键:

$$\frac{17 + n}{2} = 8 + n \implies n = 1.$$

在形成的心磷脂中, 这个氢使中央甘油的羟基完整。两个磷酸基上的氢已包含在片段  $b$  中。

### 5.2 一 PL1、其立体化学以及 Y 的稳定作用

按题目要求绘制结构时, 采用一个中央甘油单元, 其两端的羟基形成磷酸酯。它的仲羟基保持游离。

每个磷酸基团具有:

- 一个  $\text{P=O}$  键;
- 一个酸性  $\text{P-OH}$  基团;
- 一个与中央甘油相连的酯键;
- 一个与外侧甘油末端氧原子相连的酯键。

每个外侧甘油均带有两个脂肪酰基酯基: 一个位于仲羟基的氧原子上, 另一个位于其余的末端氧原子上。这恰好使用了三个甘油片段、两个磷酸片段、四个酰基片段以及一个额外的氢。

两个外侧甘油立体中心必须具有相同的绝对构型: 可以是答案中 SMILES 所编码的 ( $S, S$ ), 也可以是 ( $R, R$ )。这两种结构互为对映异构体。由于两条臂相同, 中性 PL1 的中央甘油碳原子不是立体中心。外侧构型相反时, 则可形成题目所述的具有内部镜面对称性的非手性结构。

对于 Y, 移去一个磷酸基团的质子, 并使中央头基折叠, 形成如下氢键序列



中央氧原子接受第一个氢键, 并提供第二个氢键。这些相互作用与甘油-磷酸的共价骨架共同闭合成两个由氢键形成的七元环, 每个环的计数均包含桥连氢原子。

这种协同氢键作用使单阴离子稳定。移去剩余的磷酸基团质子会消除一个氢键供体, 并在紧凑的头基中产生第二个负电荷。因此, 第二次去质子化明显更难发生:

$$pK_{a_2} \gg pK_{a_1}.$$

SMILES 指明了连接关系、形式电荷以及一种质子定域的立体化学表示; 它并不编码这种折叠构象或氢键。

### 5.3 一 脂肪酸的分子式

还原性臭氧分解会将原有的羧基保留在一种产物中。由于每个脂肪酸分子只有一个羧基, 因此每个分子只生成一分子含羧基产物。

三种产物的物质的量相等, 因此每个脂肪酸分子生成三个片段。对于无环脂肪酸, 这要求分子含有两个碳碳双键。

因此, 含有  $c$  个碳原子和两个碳碳双键的无环一元羧酸, 其分子式为

$$\text{C}_c\text{H}_{2c-4}\text{O}_2.$$

令  $B$  表示  $\sigma$  键和  $\pi$  键的总数, 其中一个双键计为两个键。根据通常的化合价,

$$B_{\text{fatty acid}} = \frac{4c + (2c - 4) + 2(2)}{2} = 3c.$$

水解过程中的小分子包括水  $\text{O}$ 、甘油  $\text{OCC(O)CO}$  和磷酸  $\text{OP(=O)(O)O}$ 。它们的键总数为

$$B_{\text{H}_2\text{O}} = 2, \quad B_{\text{glycerol}} = 13, \quad B_{\text{H}_3\text{PO}_4} = 8.$$

配平后的水解反应为



水解将每个酯键替换为两个与水中原子形成的键, 使该方程式两侧的键级总和保持相等。因此

$$\begin{aligned}255 + 8(2) &= 4B_{\text{fatty acid}} + 2(8) + 3(13), \\271 &= 4B_{\text{fatty acid}} + 55, \\B_{\text{fatty acid}} &= 54.\end{aligned}$$

所以,

$$3c = 54, \quad c = 18,$$

且

$$\boxed{\text{RCOOH} = \text{C}_{18}\text{H}_{32}\text{O}_2}.$$

作为独立核验, 由水解产物缩合可得

$$\text{PL}_1 = \text{C}_{81}\text{H}_{142}\text{O}_{17}\text{P}_2.$$

其键总数为

$$B_{\text{PL1}} = \frac{4(81) + 142 + 2(17) + 5(2)}{2} = \boxed{255}.$$

这里磷的键级总和为五, 与所给的  $\text{P}=\text{O}$  结构图一致。

答案中的亚油酸 SMILES 是一个符合条件的代表性结构。仅确定分子式, 并不能确定其具体的双键位置或  $Z$  构型。

#### 5.4 — X 的鉴定

使用所给的原子质量,

$$M(\text{C}_{18}\text{H}_{32}\text{O}_2) = 18(12.01) + 32(1.008) + 2(16.00) = 280.436 \text{ g mol}^{-1}.$$

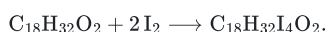
碘为  $\text{I}_2$ , SMILES 为  $\text{II}$ , 其摩尔质量为

$$M(\text{I}_2) = 253.8 \text{ g mol}^{-1}.$$

每摩尔脂肪酸消耗的碘的物质的量为

$$\frac{n(\text{I}_2)}{n(\text{fatty acid})} = \frac{181.0/253.8}{100/280.436} = 2.000.$$

这与在两个双键上发生加成一致:



含碘的卤素互化物发生加成时, 每个脂肪酸分子与两个试剂分子反应, 引入两个碘原子。因此

$$0.3657 = \frac{2(126.9)}{280.436 + 2M(X)}.$$

解得,

$$M(X) = \frac{253.8/0.3657 - 280.436}{2} = 206.79 \text{ g mol}^{-1}.$$

扣除一个碘原子所占的质量后, 剩余部分为

$$206.79 - 126.9 = 79.89 \text{ g mol}^{-1},$$

与溴的数值  $79.90 \text{ g mol}^{-1}$  相符。因此,

$$\boxed{X = \text{IBr}},$$

即一溴化碘,  $\text{IBr}$ 。

配平后的加成反应为



核验碘的质量分数,

$$w_1 = \frac{253.8}{280.436 + 2(126.9 + 79.90)} = 0.365687 \approx \boxed{36.57\%}.$$

对于符合条件的代表性分子亚油酸, 加成产物的构造表示为 **9,10,12,13-四碘十八烷酸**, CCCCC(I)C(I)CC(I)C(I)CCCCCCC(=O)O, 以及 **9,12-二溴-10,13-二碘十八烷酸**, CCCCC(I)C(Br)CC(I)C(Br)CCCCCCC(=O)O。这些 SMILES 未指定加成产物的立体化学; 立体化学以及卤素互化物加成时其他可能的区域化学取向均不影响质量计算。

#### 5.5 — 质子化后的脂质相

两个磷酸基团均被质子化后, 极性头基的静电排斥和水合作用减弱, 其有效横截面积减小。四条烃链尾部仍保持较大的体积。

因此, 堆积参数

$$p = \frac{v}{a_0 l_c}$$

随着头基面积  $a_0$  的减小而增大。这有利于脂质围绕水相通道弯曲, 并形成**反六方相**。

勾选 (d)。在该图中, 极性头基朝向内侧充满水的圆柱形通道, 而烃链尾部向外伸入周围的脂质区域。

#### 5.6 — PL2 和 PL3 的结构

对于 **PL2**, 将其水解反应与 **PL1** 的水解反应比较。脂肪酸、磷酸和水的系数不变; 一个甘油分子被  $Z$  替代。因此,

$$B(Z) - B(\text{glycerol}) = B(\text{PL2}) - B(\text{PL1}) = -1,$$

所以

$$B(Z) = 13 - 1 = \boxed{12}.$$

对于无环饱和二元醇  $C_kH_{2k+2}O_2$ ,

$$B(Z) = \frac{4k + (2k + 2) + 4}{2} = 3k + 3.$$

因此

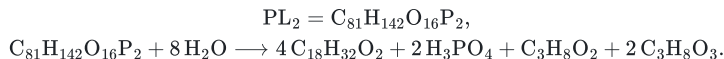
$$3k + 3 = 12 \implies k = 3.$$

所要求的对称性使两个羟基位于等价的末端位置, 得到**丙烷-1,3-二醇**,  $HOCH_2CH_2CH_2OH$ , occco。

另一种中央含羰基的结构, 即**二羟基丙酮**, occ(=o)co, 相较于甘油也会使键总数减少一, 但它会发生催化加氢。题目所述的不反应性质排除了这一结构。

因此, 绘制 **PL2** 时, 将 PL1 中央的  $-CH(OH)-$  基团替换为  $-CH_2-$ , 并保留两个外侧甘油原有的构型。这样得到 **2'-脱氧心磷脂**, 其 SMILES 已列于答案中。将中央羟基替换为氢可提高对称性, 包括形成一种具有二重旋转对称性的构象, 该旋转可使两个相同的半部互换。

其中性分子式及配平后的水解反应为



从 PL1 中移去一个氧原子, 使键级总和减少一:

$$B_{PL2} = \frac{4(81) + 142 + 2(16) + 5(2)}{2} = \boxed{254}.$$

对于 **PL3**, 由水解产物可知它含有两个脂肪酰基、一个甘油、一个磷酸基团以及乙醇 cco。

画出一个甘油, 使其仲羟基氧原子和一个末端氧原子形成脂肪酰基酯。将另一个末端氧原子连接至磷酸基团, 再将乙醇通过氧原子连接至同一个磷酸基团。该磷酸基团保留一个酸性羟基:



这就是**磷脂酰乙醇**。其中性酸形式的一个对映异构体为

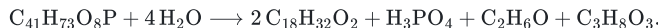


在生理 pH 下, 其剩余的磷酸羟基去质子化, 形成答案中所示的单阴离子。如果磷酸基团连接在甘油中央的氧原子上, 而两个末端氧原子连接相同的酰基, 则会得到非手性结构; 题目所述的对映异构体排除了这种情况。

需要水解的键包括两个羧酸酯键和两个磷酸酯键, 因此需要四个水分子:

$$m = \boxed{4}.$$

对于中性酸形式, 配平后的方程式为



解答已与官方解答核对。

## 题目 6: 碳纳米环

### T6. 碳纳米环

7%

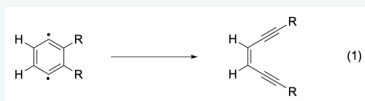
| 6.1 | 6.2 | 6.3 | 6.4 | 6.5 | 6.6 | 6.7 | $\Sigma$ |
|-----|-----|-----|-----|-----|-----|-----|----------|
| 10  | 11  | 2   | 12  | 24  | 20  | 4   | 83       |

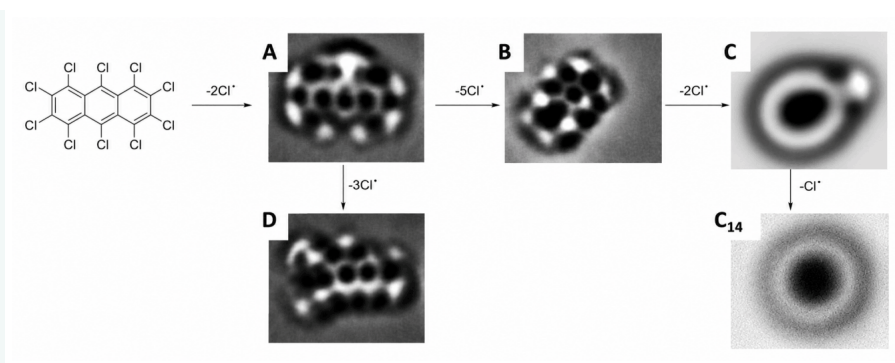
2019 年, 人们检测到了  $C_{18}$ , 它是一类称为环[n]碳 ( $C_n$ ) 的新型碳同素异形体的首个实例。环碳是具有高应变能、低稳定性的单环全碳化合物。它们可以通过具有化学键分辨能力的原子力显微镜 (AFM) 生成和分析。环碳的  $\pi$  体系赋予其有趣的芳香性。 $C_{13}$  存在三重态 ( $^3C_{13}$ , 自旋  $S = 1$ ) 和单重态 ( $^1C_{13}$ , 自旋  $S = 0$ ) 两种形式。

**6.1** 根据休克尔规则, 在表中填入  $C_{18}$ 、 $C_{16}$ 、 $^3C_{13}$  和  $^1C_{13}$  各自所含的独立芳香性 (A) 和反芳香性 (AA)  $\pi$  体系的数目。填满所有空格。10.0 分

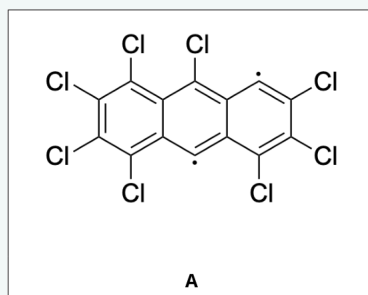
|    | $C_{18}$ | $C_{16}$ | $^3C_{13}$ | $^1C_{13}$ |
|----|----------|----------|------------|------------|
| A  |          |          |            |            |
| AA |          |          |            |            |

此后, 人们通过在表面上结合脱卤反应和逆 Bergman 反应 (1), 生成了环[n]碳  $C_{10}$ 、 $C_{12}$ 、 $C_{14}$ 、 $C_{20}$  和  $C_{26}$ 。下图为合成  $C_{14}$  过程中拍摄的 AFM 图像:





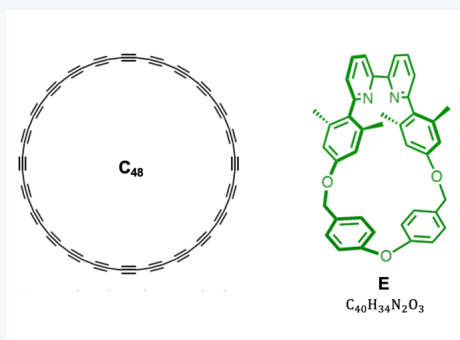
6.2 画出 B-D 的结构。注意，它们可能含有一个或多个未成对电子。已给出 A 的结构作为示例。11.0 分



6.3 在 AFM 介导的  $C_n$  合成过程中，所施加的电压可以不同。利用所给的 C-X 键能，选择在 2.5 V 电压作用于电子时，可通过逆 Bergman 反应合成  $C_{18}$  的卤代反应物中可能含有的卤素。2.0 分

| 键 (C-X) | 键解离能 / $\text{kJ mol}^{-1}$ |
|---------|-----------------------------|
| C-F     | 467                         |
| C-Cl    | 346                         |
| C-Br    | 290                         |
| C-I     | 228                         |

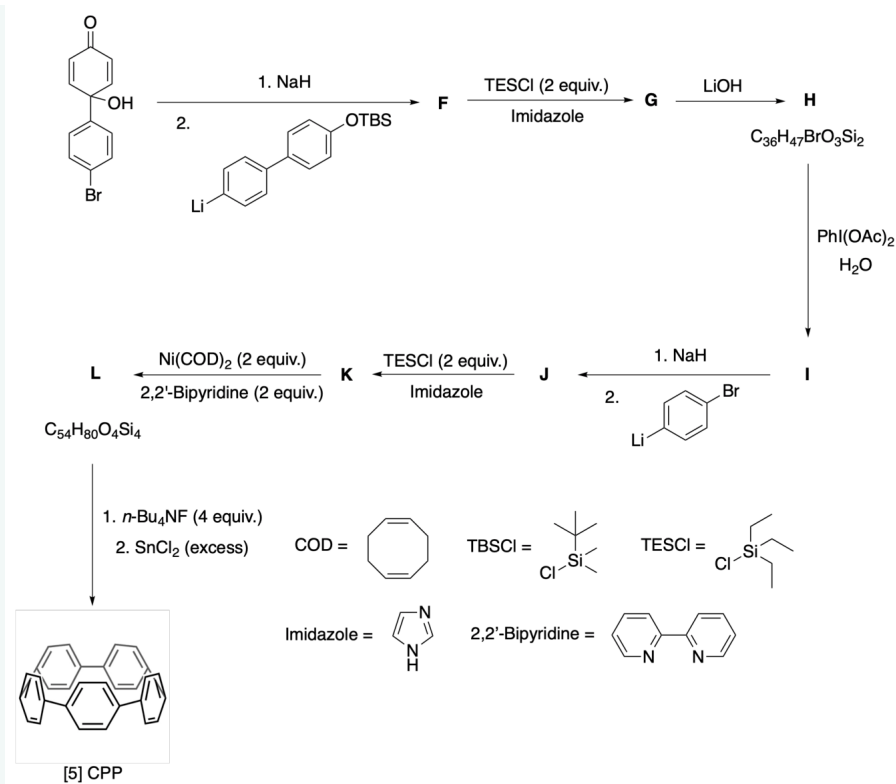
2025 年，人们合成了首个相对稳定的环[48]碳。该分子通过与大环 E 形成索烃（形成相互套连的环）而得到稳定，并首先通过正离子模式电喷雾质谱进行了表征。



6.4 在所得质谱中，观察到四个强峰，其  $m/z$  分别为 591、783、879 和 1174。推测这些离子的组成。使用整数原子质量，并假设未发生碎裂。已给出  $m/z = 591$  对应的离子作为示例。12.0 分

| $m/z$ | 591                       | 783 | 879 | 1174 |
|-------|---------------------------|-----|-----|------|
|       | $[\text{E} + \text{H}]^+$ |     |     |      |

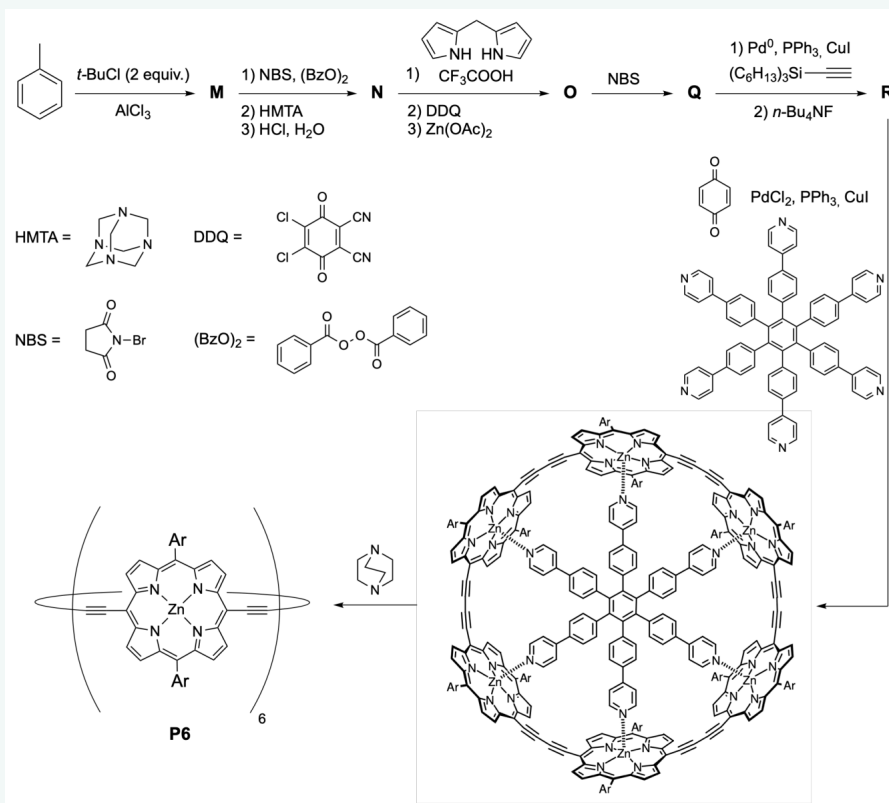
环对苯撑（CPP）是另一类具有高应变的环状分子，通常称为碳纳米箍。已知最小成员 [5]CPP 的合成路线如下，其中  $\text{PhI}(\text{OAc})_2$  作为双电子氧化剂。



(equiv. = 当量, excess = 过量)

#### 6.5 画出 F-L 的结构。24.0 分

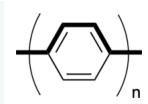
利用模板合成法，由卟啉环和三键构筑了新一代纳米带。提示：M 是热力学产物，具有四类质子。



(equiv. = 当量)

#### 6.6 画出 M-R 的结构。20.0 分

将芳香环连接成大环后，氧化或还原可使其产生全局芳香性，此时  $\pi$  电子沿整个大环离域。只有构成环周连续共轭路径的  $\pi$  体系才参与这种离域。例如，[n]CPP 在得到或失去电子后可表现出全局芳香性。 $\pi$  电子数仅沿下图中加粗的路径计数。



P6 被氧化时，可表现出全局芳香性和全局反芳香性。

6.7 根据休克尔规则，求出为使 P6 获得全局芳香性而至少应移除的电子数  $n(e)$ 。写出该全局芳香体系中的  $\pi$  电子总数  $n(t)$ 。4.0 分

#### 物理常数与方程

##### 常数

| 常数           | 数值                                               |
|--------------|--------------------------------------------------|
| 阿伏伽德罗常数      | $N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$    |
| 摩尔气体常数       | $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$    |
| 法拉第常数        | $F = 96485 \text{ C mol}^{-1}$                   |
| 普朗克常数        | $h = 6.626 \times 10^{-34} \text{ J s}$          |
| 真空光速         | $c = 2.998 \times 10^8 \text{ m s}^{-1}$         |
| 电子质量         | $m_e = 9.109 \times 10^{-31} \text{ kg}$         |
| 电子电荷         | $e = 1.602 \times 10^{-19} \text{ C}$            |
| 标准压力         | $P^\circ = 1 \text{ bar} = 10^5 \text{ Pa}$      |
| 25 °C 时水的离子积 | $K_w = 1.00 \times 10^{-14}$                     |
| 摄氏温标的零点      | $0^\circ\text{C} = 273.15 \text{ K}$             |
| 电子伏特         | $1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}$ |
| 瓦特           | $1 \text{ W} = 1 \text{ J s}^{-1}$               |
| 库仑           | $1 \text{ C} = 1 \text{ A s}$                    |
| 纳米           | $1 \text{ nm} = 1 \times 10^{-9} \text{ m}$      |
| 埃            | $1 \text{ \AA} = 1 \times 10^{-10} \text{ m}$    |
| 公吨           | $1 \text{ ton} = 1000 \text{ kg}$                |
| 升            | $1 \text{ L} = 1 \text{ dm}^3$                   |

题目译自官方英文原文。

#### 答案

此处所述结构均在相应的解答条目中以 SMILES 明确表示。

- 6.1: 按  $\text{C}_{18}$ 、 $\text{C}_{16}$ 、 $^3\text{C}_{13}$ 、 $^1\text{C}_{13}$  的顺序：  
A: 2, 0, 0, 1。  
AA: 0, 2, 0, 1。
- 6.2:  
B: 与苯环稠合且含有四个三键的十元环；保留的苯型环在 C5、C6 和 C7 位带有氯原子，C8 位为自由基中心。分子式为  $\text{C}_{14}\text{Cl}_3$ ，含一个未成对电子。  
C: 单环  $\text{C}_{14}\text{Cl}$  自由基，含有六个三键和一对相邻的  $\text{C}(\text{Cl})=\text{C}^\bullet$  碳原子。  
D: 1,6,7-三氯-2,3-双(氯乙炔基)萘-4,5,8-三基， $\text{C}_{14}\text{Cl}_5$ ，含三个未成对电子。
- 6.3:  $X = \text{I}$ ，仅碘。
- 6.4:  
591:  $[\text{E} + \text{H}]^+$ 。  
783:  $[\text{C}_{48} + 3\text{E} + 3\text{H}]^{3+}$ 。  
879:  $[\text{C}_{48} + 2\text{E} + 2\text{H}]^{2+}$ 。  
1174:  $[\text{C}_{48} + 3\text{E} + 2\text{H}]^{2+}$ 。
- 6.5:  
F: 由 TBS 保护的联苯基锂试剂加成形成的顺式环己二烯二醇。  
G: F 的双 TES 醚。  
H: 通过选择性脱除 TBS 得到的末端酚。  
I: 由 H 经氧化去芳构化得到的末端对醌醇。  
J: 4-溴苯基锂与 I 加成形成的第二个顺式二醇。  
K: 四个羟基均由 TES 保护的二溴化物。  
L: K 的两个末端溴代芳基碳原子偶联形成的环状产物。
- 6.6:  
M: 3,5-二叔丁基甲苯。  
N: 3,5-二叔丁基苯甲醛。  
O: 5,15-双(3,5-二叔丁基苯基)卟啉锌(II)。  
Q: O 的 10,20-二溴衍生物。  
R: O 的 10,20-二乙炔基衍生物。

• 6.7:  $n(e) = 2, \quad n(t) = 82$ 。

## 解答

### 6.1 一对两个相互垂直的 $\pi$ 体系分别计数

每个环碳均具有两组相互垂直的  $\pi$  轨道：一组垂直于分子平面，另一组位于分子平面内。

对每个体系分别应用休克尔电子计数判据：

$$4k + 2 \pi \text{ 电子：芳香性}, \quad 4k \pi \text{ 电子：反芳香性}.$$

此处所考虑的理想化组态中的电子分布如下：

| 物种           | 两个体系中的 $\pi$ 电子数 | A | AA |
|--------------|------------------|---|----|
| $C_{18}$     | 18, 18           | 2 | 0  |
| $C_{16}$     | 16, 16           | 0 | 2  |
| ${}^3C_{13}$ | 13, 13           | 0 | 0  |
| ${}^1C_{13}$ | 14, 12           | 1 | 1  |

对于  $C_{18}$ ,  $18 = 4(4) + 2$ , 因此两个体系均具有芳香性。对于  $C_{16}$ ,  $16 = 4(4)$ , 因此两个体系均具有反芳香性。

在三重态  $C_{13}$  组态中, 每个体系的电子数均为奇数, 且各有一个未成对电子; 两者均不满足上述闭壳层休克尔电子数条件。在电子配对的单重态组态中, 26 个  $\pi$  电子分配为 14 个和 12 个, 得到一个芳香性体系和一个反芳香性体系。

### 6.2 开环中间体

逆 Bergman 反应断裂原有稠合骨架中的 C—C 键, 并生成新的三键。必须同时考虑氯原子的脱除和碳的化合价。

在下列 SMILES 中, 方括号内的 [c] 和 [C] 原子通过其明确未满足的价态标示碳自由基。

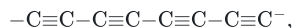
#### B — 三氯取代的苯并环癸四炔自由基

SMILES: C1c1c(Cl)c(Cl)[c]c2c1C#CC#CC#CC#C2

保留一个六元苯型环。其四个非稠合位置依次编号为 C5—C8, 分别带有：

- C5: 氯原子;
- C6: 氯原子;
- C7: 氯原子;
- C8: 一个未成对电子, 该位置与一个稠合碳原子相邻。

两个稠合碳原子还通过以下八碳链相连

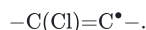


形成一个稠合的十元环。因此, B 含有四个三键、三个氯原子和一个自由基中心, 分子式为  $C_{14}Cl_3$ 。

#### C — 一氯环[14]碳自由基

SMILES: C1C1=[C]C#CC#CC#CC#CC#CC#CC#C1

画出一个十四元单碳环, 其中含有六个交替分布的三键和一个双键。双键的一个碳原子带有氯原子, 另一个带有未成对电子：



这些不饱和单元之间的其余键均为单键。因此, C 的分子式为  $C_{14}Cl$ , 自由基中心位于连有氯原子的碳原子旁边。

#### D — 1,6,7-三氯-2,3-双(氯乙炔基)萘-4,5,8-三基

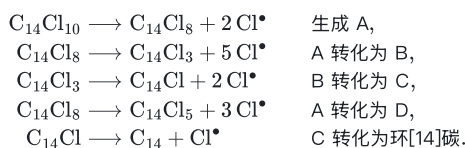
SMILES: C1c1c(C#CCl)c(C#CCl)[c]c2[c]c(Cl)c(Cl)[c]c12

采用萘的标准编号：

- C2 和 C3 各带有一条氯乙炔基支链  $-C\equiv C-Cl$ 。
- C1、C6 和 C7 各带有一个氯原子。
- C4、C5 和 C8 各带有一个未成对电子。

萘核保持完整, 而第三个环开环后形成两条氯乙炔基支链。其分子式为  $C_{14}Cl_5$ , 含有三个自由基中心。

图示反应序列的氯原子收支如下：



最终的环[14]碳具有七个交替分布的三键。

名称：环[14]碳。

SMILES: C1#CC#CC#CC#CC#CC#CC#C1

### 6.3 电子能量与键解离

一个电子经过电势差  $U$  加速后获得能量  $eU$ 。对于每摩尔电子,

$$E_{\text{mol}} = FU = (96\,485 \text{ C mol}^{-1})(2.5 \text{ J C}^{-1}) = 241\,212.5 \text{ J mol}^{-1}.$$



末端酚的 TBS 醚仍然保留。

#### H — G 经选择性 TBS 脱保护得到的末端酚

SMILES: BrC1ccc([C@]2(O[Si](CC)(CC)CC)C=C[C@](O[Si](CC)(CC)CC)(C3ccc(-C4ccc(O)cc4)cc3)C=C2)cc1

LiOH 使酚的 TBS 醚水解:



两个叔醇的 TES 醚保留。所得分子式恰好与题目所给一致:

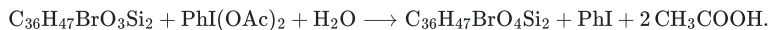


#### I — H 经氧化去芳构化形成的末端对醌醇

SMILES: BrC1ccc([C@]2(O[Si](CC)(CC)CC)C=C[C@](O[Si](CC)(CC)CC)(C3ccc(C4(O)C=CC(=O)C=C4)cc3)C=C2)cc1

末端酚转变为环己-2,5-二烯-1-酮。其对位碳原子原本已连接分子的其余部分,此时再引入一个 OH 基团。

该双电子氧化反应的配平方程式为



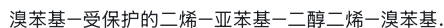
因此, I 含有原有的受保护环己二烯单元和一个新的羟基环己二烯酮单元。

#### J — 第二个顺式二醇加成产物

SMILES: BrC1ccc([C@]2(O[Si](CC)(CC)CC)C=C[C@](O[Si](CC)(CC)CC)(C3ccc([C@]4(O)C=C[C@](O)(C5ccc(Br)cc5)C=C4)cc3)C=C2)cc1

NaH 使 I 中新形成的 OH 基团去质子化。随后, 4-溴苯基锂加成至剩余的酮羰基, 过程与 F 的形成相同。

此时, 含五个环的链具有如下排列顺序



J 的分子式为  $\text{C}_{42}\text{H}_{52}\text{Br}_2\text{O}_4\text{Si}_2$ 。

#### K — 四个羟基均由 TES 保护的二溴前体

SMILES: BrC1ccc([C@]2(O[Si](CC)(CC)CC)C=C[C@](O[Si](CC)(CC)CC)(C3ccc([C@]4(O[Si](CC)(CC)CC)C=C[C@](O[Si](CC)(CC)CC)(C5ccc(Br)cc5)C=C4)cc3)C=C2)cc1

再用两当量 TESCO 保护 J 的两个游离羟基。因此, K 含有四个 TES 醚和两个末端芳基溴基团:



#### L — 四个羟基均由 TES 保护、两个环己去芳构化的 [5]环对苯撑

SMILES: c1%10ccc([C@]2(O[Si](CC)(CC)CC)C=C[C@](O[Si](CC)(CC)CC)(C3ccc([C@]4(O[Si](CC)(CC)CC)C=C[C@](O[Si](CC)(CC)CC)(C5ccc-%10cc5)C=C4)cc3)C=C2)cc1

镍导的分子内偶联将原先连接溴原子的两个芳香碳原子连接起来, 从而闭合形成由五个单元组成的环箍。

总偶联反应的配平方程式为



所得分子式与题目一致:

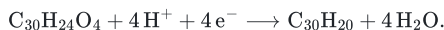


图示的两当量镍配合物是实验中的试剂用量; 按总氧化还原反应的计量关系, 消耗一当量  $\text{Ni}(0)$ 。

最后, 氟离子脱除全部四个 TES 基团。对于每个基团, 水解后处理可表示为



所得四醇的分子式为  $\text{C}_{30}\text{H}_{24}\text{O}_4$ 。随后经还原芳构化得到 [5]CPP。其配平的还原半反应方程式为



锡(II) 提供电子:



名称: [5]环对苯撑。

SMILES: c1%10ccc(-c2ccc(-c3ccc(-c4ccc(-c5ccc-%10cc5)cc4)cc3)cc2)cc1

### 6.6 — 卟啉构筑单元

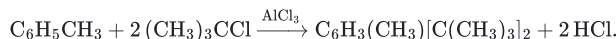
此处定义 Ar 为 3,5-二叔丁基苯基。

#### M — 3,5-二叔丁基甲苯

SMILES: Cc1cc(C(C)(C)C)cc(C(C)(C)C)c1

在热力学控制的烷基化条件下, 大体积取代基采取交替的 1,3,5 排列, 避免甲基与叔丁基相邻取代。

总烷基化反应为



M 具有题目要求的四种质子环境:

1. 甲基, 3 H;
2. 两个等价的叔丁基, 18 H;
3. 芳环上的 H2 和 H6, 2 H;

4. 芳环上的 H4, 1 H。

#### N — 3,5-二叔丁基苯甲醛

SMILES: O=Cc1cc(C(C)(C)C)cc(C(C)(C)C)c1

NBS 在过氧化物引发剂存在下使苄位甲基发生溴化：



该中间体为 3,5-二叔丁基溴化苄。

SMILES: BrCc1cc(C(C)(C)C)cc(C(C)(C)C)c1

先用 HMTA 处理，再进行酸性水解，通过 Sommelet 反应转化为醛。将胺类水解产物写成中性形式，得到配平的总反应方程式



在酸性反应介质中，胺被质子化。

#### O — 5,15-双(3,5-二叔丁基苯基)卟啉锌(II)

SMILES: CC(C)(C)c1cc(-c2c3[n]4->[Zn+2]56<-[n]7c(cc8ccc2[n-]->58)C=Cc7c(-c2cc(C(C)(C)C)cc(C(C)(C)C)c2)c2ccc(cc4C=C3)[n-]->62)cc(C(C)(C)C)c1

两个醛分子与两个二吡咯甲烷分子构成卟啉骨架。来自醛的碳原子成为两个彼此相对、带有 Ar 的中位碳原子。另外两个中位保留氢原子。

缩合及 DDQ 氧化的总配平方程式为



随后，锌的嵌入取代两个内侧 N-H 质子：



该 SMILES 明确包含从 N 指向 Zn 的配位键。四个卟啉氮原子以近似平面正方形的排列方式与锌配位；SMILES 本身并未指定这一几何构型。

#### Q — 10,20-二溴-5,15-双(3,5-二叔丁基苯基)卟啉锌(II)

SMILES: CC(C)(C)c1cc(-c2c3[n]4->[Zn+2]56<-[n]7c(c(Br)c8ccc2[n-]->58)C=Cc7c(-c2cc(C(C)(C)C)cc(C(C)(C)C)c2)c2ccc(c(Br)c4C=C3)[n-]->62)cc(C(C)(C)C)c1

NBS 将剩余的两个中位氢原子替换为溴原子。总配平方程式为



#### R — 10,20-二乙炔基-5,15-双(3,5-二叔丁基苯基)卟啉锌(II)

SMILES: C#Cc1c2[n]3->[Zn+2]45<-[n]6c(c(C#C)c7ccc(c(-c8cc(C(C)(C)C)cc(C(C)(C)C)c8)c3C=C2)[n-]->47)C=Cc6c(-c2cc(C(C)(C)C)cc(C(C)(C)C)c2)c2ccc1[n-]->52

每个中位溴代位点均与三己基硅基保护的乙炔发生 Sonogashira 偶联：



其中 P 表示其余的卟啉骨架。

随后，氟离子脱除两个硅基保护基。对于每个乙炔基，

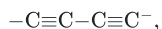


因此，R 含有两个彼此相对的末端乙炔基，分子式为  $\text{C}_{52}\text{H}_{52}\text{N}_4\text{Zn}$ 。这些末端基团随后发生氧化偶联，生成 P6 中连接卟啉的丁二炔连接基。

### 6.7 — 全局 $\pi$ 电子计数

仅计入属于环绕整个纳米环的一条连续共轭路径的轨道。

每个卟啉沿其两个相对且带有连接基的中位之间的路径贡献 10 个  $\pi$  电子。每个丁二炔桥，



贡献 4 个  $\pi$  电子：每个三键的两个相互垂直的  $\pi$  体系中，只有一个属于全局共轭路径。

对于六个卟啉和六个丁二炔桥，

$$N_\pi = 6(10) + 6(4) = 84.$$

移除  $n(e)$  个电子后，休克尔条件为

$$84 - n(e) = 4k + 2.$$

移除一个电子后为 83，不满足该条件。移除两个电子后得到

$$82 = 4(20) + 2.$$

因此，根据题目要求的休克尔电子计数判据，

$$\boxed{n(e) = 2, \quad n(t) = 82}.$$

解答已与官方解答核对。

## 题目 7：固氮

### T7. 固氮

7%

|     |     |     |     |     |     |     |          |
|-----|-----|-----|-----|-----|-----|-----|----------|
| 7.1 | 7.2 | 7.3 | 7.4 | 7.5 | 7.6 | 7.7 | $\Sigma$ |
| 3   | 8   | 15  | 3   | 6   | 6   | 13  | 54       |

哈伯-博施法是工业生产氨的主要方法。下图为合成氨工厂的简化流程图。

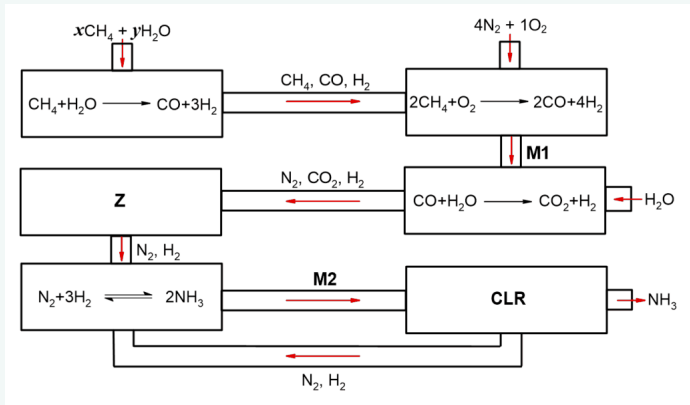


图 1. M1 – 混合物 1, M2 – 混合物 2, Z – CO<sub>2</sub> 洗涤器, CLR – 冷却器

在以下计算中, 假设图 1 中除生成 NH<sub>3</sub> 的反应外, 所有反应均定量进行。

7.1 勾选 M1 和 M2 中所含的气体; 并勾选  $x$  与  $y$  之间的正确关系。3.0 分

|    | CH <sub>4</sub> | H <sub>2</sub> O | CO | O <sub>2</sub> | H <sub>2</sub> | N <sub>2</sub> | NH <sub>3</sub> | CO <sub>2</sub> |
|----|-----------------|------------------|----|----------------|----------------|----------------|-----------------|-----------------|
| M1 |                 |                  |    |                |                |                |                 |                 |
| M2 |                 |                  |    |                |                |                |                 |                 |

|         |         |         |
|---------|---------|---------|
| $x > y$ | $x = y$ | $x < y$ |
|         |         |         |

乌兹别克斯坦的 Navoiyazot 工厂投产了一套年产能 660,000 吨的合成氨装置, 其总收率为 97.0%。

7.2 若 Navoiyazot 按照图 1 所示流程运行, 计算每年生产 660,000 吨氨所需的 CH<sub>4</sub> 质量 (吨)。8.0 分

考虑一个包含反应物循环利用的实际反应体系模型。该开放体系以循环模式运行。每个循环包含四个步骤:

1. 每个循环结束后, 向反应器中加入总物质的量为  $n_0$  mol、化学计量比为 N<sub>2</sub> : H<sub>2</sub> = 1 : 3 的混合气体。
2. 反应以恒定收率  $\eta = 0.150$  进行。
3. 通过液化分离氨。
4. 将未反应的气体返回反应器。

重复此循环, 直至达到所需的总收率。

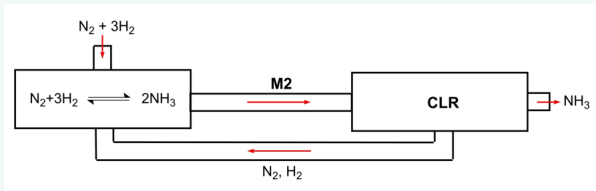


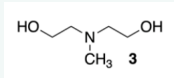
图 2. M2. – 混合物 2, CLR – 冷却器。

7.3

a) 若  $n_0 = 4$  mol, 计算第 58 个循环结束后 (加入第 59 份混合气体之前) 体系中氮气的物质的量。结果保留 4 位小数。提示: 需要用到等比数列的求和公式。

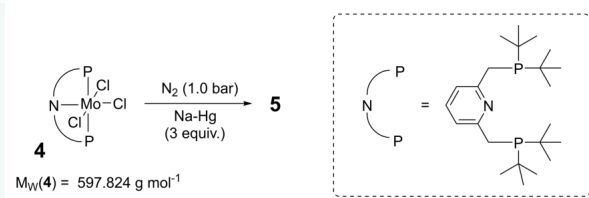
b) 计算将总收率从 15.0% 提高到 97.0% 所需的循环次数。15.0 分

使用 3 的水溶液从混合物中除去 CO<sub>2</sub>。



7.4 写出该反应的方程式。3.0 分

按照下列反应路线, 通过固定分子氮得到配合物 5。



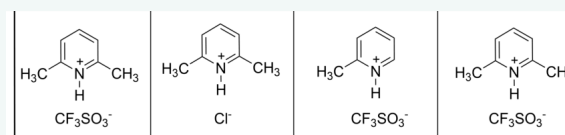
7.5 使用配体的简化表示法，画出 5 的结构。已知 1.00 g 4 恰好与 273.15 K、1.0 bar 下的  $94.97 \text{ cm}^3 \text{ N}_2$  按化学计量比反应。6.0 分

研究了不同还原剂和添加剂对  $\text{NH}_3$  收率的影响。下表列出了不同的 Red 和 Ad 组合、各自的  $E^\circ$  和  $pK_a$ ，以及所得的  $\text{NH}_3$  产量。

Red



Ad



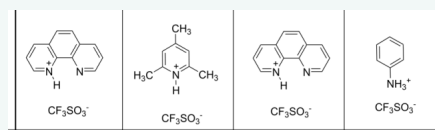
| #                     | 1     | 2     | 3     | 4     |
|-----------------------|-------|-------|-------|-------|
| $E^\circ$ (V)         | -0.88 | -1.15 | -1.15 | -1.15 |
| $pK_a$                | 14.4  | 14.4  | 13.9  | 14.4  |
| $\text{NH}_3$ 产量 (摩尔) | 0     | 0.7   | 9.1   | 11.8  |

7.6 按氨收率从高到低的顺序，对下列 Red/Ad 组合 A–D 排序。6.0 分

Red



Ad



| #             | A     | B     | C     | D     |
|---------------|-------|-------|-------|-------|
| $E^\circ$ (V) | -0.09 | -1.10 | -1.10 | -1.10 |
| $pK_a$        | 13.7  | 15.0  | 13.7  | 10.6  |

固氮也可以通过二元氮化物（含有  $\text{N}^{3-}$  的化合物）实现。由纯单质制得了此类氮化物 7、8、9。将它们与  $\text{SiO}_2$  一起加热时，会生成稳定化合物 10 的红色晶体，且该化合物是唯一产物。能够描述化合物 10 结构的最简式为  $\text{Q}_\alpha \text{R}_\beta \text{S}_2 \text{T} [\text{Si}_{12} \text{N}_{24}]$ 。此外：

- 氮的质量分数为  $w(\text{N})_7 = 9.16\%$ 、 $w(\text{N})_8 = 18.90\%$ 、 $w(\text{N})_9 = 39.94\%$
- Q 和 R 是处于其最高氧化态的金属阳离子。
- S 是单原子阴离子。
- T 是具有四面体构型的阴离子。
- 为使 10 定量生成，质量比为  $7 : 8 : 9 : \text{SiO}_2 = 5.09 : 2.96 : 3.27 : 1.00$ 。

7.7 确定 7–10 的实验式。写明阴离子 S 和 T 的组成。13.0 分

物理常数与方程

常数

| 常数      | 数值                                            |
|---------|-----------------------------------------------|
| 阿伏伽德罗常数 | $N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$ |
| 摩尔气体常数  | $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ |
| 法拉第常数   | $F = 96485 \text{ C mol}^{-1}$                |
| 普朗克常数   | $h = 6.626 \times 10^{-34} \text{ J s}$       |
| 真空中的光速  | $c = 2.998 \times 10^8 \text{ m s}^{-1}$      |
| 电子质量    | $m_e = 9.109 \times 10^{-31} \text{ kg}$      |
| 电子电荷    | $e = 1.602 \times 10^{-19} \text{ C}$         |

| 常数           | 数值                                               |
|--------------|--------------------------------------------------|
| 标准压力         | $P^\circ = 1 \text{ bar} = 10^5 \text{ Pa}$      |
| 25 °C 时水的离子积 | $K_w = 1.00 \times 10^{-14}$                     |
| 摄氏温标的零点      | $0^\circ\text{C} = 273.15 \text{ K}$             |
| 电子伏特         | $1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}$ |
| 瓦特           | $1 \text{ W} = 1 \text{ J s}^{-1}$               |
| 库仑           | $1 \text{ C} = 1 \text{ A s}$                    |
| 纳米           | $1 \text{ nm} = 1 \times 10^{-9} \text{ m}$      |
| 埃            | $1 \text{ \AA} = 1 \times 10^{-10} \text{ m}$    |
| 公吨           | $1 \text{ ton} = 1000 \text{ kg}$                |
| 升            | $1 \text{ L} = 1 \text{ dm}^3$                   |

方程

| 方程                                                                                    | 表达式                                                                                   |
|---------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------|
| 理想气体状态方程                                                                              | $PV = nRT$                                                                            |
| 道尔顿定律                                                                                 | $P_i = x_iP$                                                                          |
| 比尔-朗伯定律                                                                               | $A = \log_{10} \frac{I_0}{I} = \epsilon cl$                                           |
| 光子的能量                                                                                 | $E = h\nu = \frac{hc}{\lambda}$                                                       |
| 热量与温度变化                                                                               | $Q = nC_m\Delta T$                                                                    |
| 吉布斯能的定义                                                                               | $G = H - TS$                                                                          |
| 吉布斯能与平衡常数                                                                             | $\Delta_r G^\circ = -RT \ln K$                                                        |
| 焓变与温度的关系（当 $\Delta_r C_p = \text{const}$ 时）                                           | $\Delta_r H_{T_2} = \Delta_r H_{T_1} + \Delta_r C_p(T_2 - T_1)$                       |
| 熵变与温度的关系（当 $\Delta_r C_p = \text{const}$ 时）                                           | $\Delta_r S_{T_2} = \Delta_r S_{T_1} + \Delta_r C_p \ln \frac{T_2}{T_1}$              |
| 亨德森-哈塞尔巴尔赫方程                                                                          | $pH = pK_a + \log_{10} \frac{[\text{A}^-]}{[\text{HA}]}$                              |
| 平均反应速率                                                                                | $r = \frac{\Delta c}{\Delta t}$                                                       |
| 速率方程                                                                                  | $r = k[\text{A}]^x[\text{B}]^y$                                                       |
| 阿伦尼乌斯定律                                                                               | $k = A \exp\left(-\frac{E_o}{RT}\right)$                                              |
| 一级反应的积分速率方程                                                                           | $c = c_0 e^{-kt}; \quad kt = \ln \frac{c_0}{c}$                                       |
| 一级反应中反应物的寿命                                                                           | $\tau = \frac{1}{k}$                                                                  |
| n 级反应的积分速率方程（ $n \neq 1$ ）                                                            | $kt = \frac{1}{n-1} \left(c^{1-n} - c_0^{1-n}\right), \text{ 其中 } n \neq 1$           |
| 连续反应中中间体的浓度： $\text{A} \xrightarrow{k_1} \text{B} \xrightarrow{k_2} \text{D}$         | $[\text{B}] = \frac{k_1[\text{A}]_0}{k_2 - k_1} \left(e^{-k_1 t} - e^{-k_2 t}\right)$ |
| 竞争反应中的产物比： $\text{A} \xrightarrow{k_1} \text{B}, \text{A} \xrightarrow{k_2} \text{C}$ | $\frac{[\text{B}]}{[\text{C}]} = \frac{k_1}{k_2}$                                     |
| 米氏方程                                                                                  | $r_0 = r_{\max} \frac{[\text{S}]_0}{K_M + [\text{S}]_0}$                              |
| 比表面积                                                                                  | $s = \frac{S}{m}$                                                                     |
| 数列：等差数列、等比数列                                                                          | $a_n = a_1 + d(n-1); \quad a_n = a_1 q^{n-1}$                                         |
| 等比数列求和                                                                                | $\sum_{k=0}^n a_1 q^k = a_1 \frac{q^{n+1} - 1}{q - 1}$                                |
| 半径为 $r$ 的球的体积                                                                         | $V = \frac{4}{3} \pi r^3$                                                             |
| 半径为 $r$ 的球的表面积                                                                        | $S = 4 \pi r^2$                                                                       |
| 底面半径为 $r$ 、高为 $h$ 的圆锥的体积                                                              | $V = \frac{1}{3} \pi r^2 h$                                                           |
| 底面半径为 $r$ 、高为 $h$ 的圆柱的体积                                                              | $V = \pi r^2 h$                                                                       |

将所有气体视为理想气体。

在平衡常数的计算中，所有浓度均以  $1 \text{ mol dm}^{-3}$  的浓度为参照。

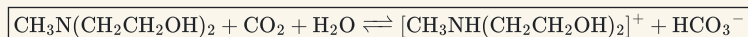
元素周期表

|                      |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   |                        |
|----------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|------------------------|
| 1<br>1<br>H<br>1.008 |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   | 18<br>2<br>He<br>4.003 |
| 3<br>Li<br>6.94      | 4<br>Be<br>9.01   |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   | 5<br>B<br>10.81   | 6<br>C<br>12.01   | 7<br>N<br>14.01   | 8<br>O<br>16.00   | 9<br>F<br>19.00   | 10<br>Ne<br>20.18      |
| 11<br>Na<br>22.99    | 12<br>Mg<br>24.30 |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   | 13<br>Al<br>26.98 | 14<br>Si<br>28.09 | 15<br>P<br>30.97  | 16<br>S<br>32.06  | 17<br>Cl<br>35.45 | 18<br>Ar<br>39.95      |
| 19<br>K<br>39.10     | 20<br>Ca<br>40.08 | 21<br>Sc<br>44.96 | 22<br>Ti<br>47.87 | 23<br>V<br>50.94  | 24<br>Cr<br>52.00 | 25<br>Mn<br>54.94 | 26<br>Fe<br>55.85 | 27<br>Co<br>58.93 | 28<br>Ni<br>58.69 | 29<br>Cu<br>63.55 | 30<br>Zn<br>65.38 | 31<br>Ga<br>69.72 | 32<br>Ge<br>72.63 | 33<br>As<br>74.92 | 34<br>Se<br>78.97 | 35<br>Br<br>79.90 | 36<br>Kr<br>83.80      |
| 37<br>Rb<br>85.47    | 38<br>Sr<br>87.62 | 39<br>Y<br>88.91  | 40<br>Zr<br>91.22 | 41<br>Nb<br>92.91 | 42<br>Mo<br>95.95 | 43<br>Tc<br>-     | 44<br>Ru<br>101.1 | 45<br>Rh<br>102.9 | 46<br>Pd<br>106.4 | 47<br>Ag<br>107.9 | 48<br>Cd<br>112.4 | 49<br>In<br>114.8 | 50<br>Sn<br>118.7 | 51<br>Sb<br>121.8 | 52<br>Te<br>127.6 | 53<br>I<br>126.9  | 54<br>Xe<br>131.3      |
| 55<br>Cs<br>132.9    | 56<br>Ba<br>137.3 | 57-71             | 72<br>Hf<br>178.5 | 73<br>Ta<br>180.9 | 74<br>W<br>183.8  | 75<br>Re<br>186.2 | 76<br>Os<br>190.2 | 77<br>Ir<br>192.2 | 78<br>Pt<br>195.1 | 79<br>Au<br>197.0 | 80<br>Hg<br>200.6 | 81<br>Tl<br>204.4 | 82<br>Pb<br>207.2 | 83<br>Bi<br>209.0 | 84<br>Po<br>-     | 85<br>At<br>-     | 86<br>Rn<br>-          |
| 87<br>Fr<br>-        | 88<br>Ra<br>-     | 89-103            | 104<br>Rf<br>-    | 105<br>Db<br>-    | 106<br>Sg<br>-    | 107<br>Bh<br>-    | 108<br>Hs<br>-    | 109<br>Mt<br>-    | 110<br>Ds<br>-    | 111<br>Rg<br>-    | 112<br>Cn<br>-    | 113<br>Nh<br>-    | 114<br>Fl<br>-    | 115<br>Mc<br>-    | 116<br>Lv<br>-    | 117<br>Ts<br>-    | 118<br>Og<br>-         |
|                      |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   |                        |
| 57<br>La<br>138.9    | 58<br>Ce<br>140.1 | 59<br>Pr<br>140.9 | 60<br>Nd<br>144.2 | 61<br>Pm<br>-     | 62<br>Sm<br>150.4 | 63<br>Eu<br>152.0 | 64<br>Gd<br>157.3 | 65<br>Tb<br>158.9 | 66<br>Dy<br>162.5 | 67<br>Ho<br>164.9 | 68<br>Er<br>167.3 | 69<br>Tm<br>168.9 | 70<br>Yb<br>173.0 | 71<br>Lu<br>175.0 |                   |                   |                        |
| 89<br>Ac<br>-        | 90<br>Th<br>232.0 | 91<br>Pa<br>231.0 | 92<br>U<br>238.03 | 93<br>Np<br>-     | 94<br>Pu<br>-     | 95<br>Am<br>-     | 96<br>Cm<br>-     | 97<br>Bk<br>-     | 98<br>Cf<br>-     | 99<br>Es<br>-     | 100<br>Fm<br>-    | 101<br>Md<br>-    | 102<br>No<br>-    | 103<br>Lr<br>-    |                   |                   |                        |

题目译自官方英文原文。

## 答案

- 7.1: 对 **M1** 勾选  $\text{CO}$ 、 $\text{H}_2$  和  $\text{N}_2$ ；对 **M2** 勾选  $\text{H}_2$ 、 $\text{N}_2$  和  $\text{NH}_3$ 。勾选  $x > y$ 。
- 7.2:  $2.80 \times 10^5$  吨 $\text{CH}_4$ 每年。
- 7.3(a):  $5.6662 \text{ mol}$ 的 $\text{N}_2$ 。
- 7.3(b): 189个循环，共计，即在达到 15.0% 收率的第一个循环之后再 进行 188 个循环。
- 7.4:



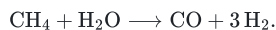
- 7.5: **5** 为  $[\text{Mo}_2(\text{L})_2(\text{N}_2)_5]$ ：两个八面体构型的钼(0)中心各配位一个三齿 PNP 配体  $\text{L}$  和两个端位双氮配体，并通过一个两端均以端接方式配位的桥联双氮配体相连接。
- 7.6: 按氨收率从高到低排列为  $\text{B} > \text{C} > \text{D} > \text{A}$ 。
- 7.7: **7** = 氮化镧(III)， $\text{LaN}$ ；**8** = 氮化钙， $\text{Ca}_3\text{N}_2$ ；**9** = 氮化硅， $\text{Si}_3\text{N}_4$ 。**10** 的实验式为  $[\text{Ca}_9\text{La}_5\text{Si}_{13}\text{N}_{25}\text{O}_5]$ ，按结构可写为  $[\text{Ca}_9\text{La}_5\text{O}_2[\text{SiNO}_3][\text{Si}_{12}\text{N}_{24}]]$ 。因此，**S** 为  $\text{O}^{2-}$ ，**T** 为四面体构型的  $[\text{SiNO}_3]^{5-}$ 。

## 解答

### 7.1 — 两种混合物中的气体

该流程中使用的分子物种为甲烷  $\text{C}$ 、水  $\text{O}$ 、一氧化碳  $[\text{C}-]\neq[\text{O}+]$ 、氧气  $\text{O}=\text{O}$ 、氢气  $[\text{H}][\text{H}]$ 、氮气  $\text{N}\neq\text{N}$ 、氨  $\text{N}$  和二氧化碳  $\text{O}=\text{C}=\text{O}$ 。

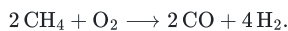
第一个反应器进行蒸汽重整反应：



其出口物流含有未反应的甲烷、一氧化碳和氢气。水已耗尽，而甲烷仍有剩余；因此，

$$x > y.$$

随后，剩余甲烷与随氮气一同引入的氧气定量反应：



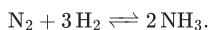
因此，在该反应器出口处，

$$\text{M1} : \text{CO}, \text{H}_2, \text{N}_2.$$

随后发生的水煤气变换反应为



洗涤器除去生成的二氧化碳，留下氮气和氢气用于合成氨：



由于合成氨反应未完全进行，该反应器的出口物流中含有产物和未反应的反应物：

$$\boxed{\text{M2 : H}_2, \text{N}_2, \text{NH}_3}.$$

不应勾选其他方框。

## 7.2 — 甲烷的年需求量

以随 4 mol 氮气一同供入的 1 mol 氧气为计算基准。

在第一个反应器中， $y$  mol 甲烷与  $y$  mol 水反应。剩余甲烷为  $x - y$  mol。第二个反应器每消耗一摩尔氧气，就消耗 2 mol 甲烷，因此

$$x - y = 2.$$

在变换反应之前，各物质的量为

$$n(\text{CO}) = y + 2, \quad n(\text{H}_2) = 3y + 4.$$

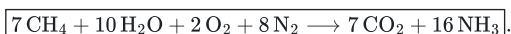
将全部一氧化碳转化为二氧化碳，会额外生成  $y + 2$  mol 氢气。因此

$$n(\text{H}_2) = 4y + 6.$$

按化学计量比合成氨时，4 mol 氮气需要 12 mol 氢气：

$$4y + 6 = 12, \quad y = 1.5, \quad x = 3.5.$$

因此，3.5 mol 甲烷可为生成 8 mol 氨提供所需的反应物。用整数系数表示，总的理论反应为



根据所给周期表计算得到的摩尔质量为

$$M(\text{CH}_4) = 12.01 + 4(1.008) = 16.042 \text{ g mol}^{-1},$$

$$M(\text{NH}_3) = 14.01 + 3(1.008) = 17.034 \text{ g mol}^{-1}.$$

考虑总收率，

$$m(\text{CH}_4) = \frac{660\,000 \text{ tons}}{0.970} \frac{7}{16} \frac{16.042}{17.034} = 280\,344.6 \text{ tons}.$$

因此，

$$\boxed{m(\text{CH}_4) = 2.80 \times 10^5 \text{ tons year}^{-1}}.$$

## 7.3(a) — 58 个循环后剩余的氮气

每份新加入的混合气体含有

$$a = \frac{n_0}{4} = 1 \text{ mol}$$

的氮气。设  $r_k$  为第  $k$  个循环结束后，已除去氨且尚未进行下一次加料时，未反应氮气的物质的量。每个循环中未反应的比例为

$$q = 1 - \eta = 0.850.$$

递推关系为

$$r_k = q(r_{k-1} + a), \quad r_0 = 0.$$

因此，

$$r_k = a(q + q^2 + \cdots + q^k) = a \frac{q(1 - q^k)}{1 - q}.$$

当  $k = 58$  时，

$$r_{58} = (1 \text{ mol}) \frac{0.85(1 - 0.85^{58})}{0.15} = 5.6662099726 \text{ mol}.$$

保留四位小数，

$$\boxed{r_{58} = 5.6662 \text{ mol of N}_2}.$$

## 7.3(b) — 达到 97.0% 总收率所需的循环次数

经过  $k$  个循环后，加入的氮气总物质的量为  $ka$ ，已转化的物质的量为  $ka - r_k$ 。因此，氨的累计收率为

$$Y_k = \frac{2(ka - r_k)}{2ka} = 1 - \frac{q(1 - q^k)}{k(1 - q)}.$$

于是

$$Y_k = 1 - \frac{0.85(1 - 0.85^k)}{0.15k}.$$

所需满足的条件为  $Y_k \geq 0.970$ 。阈值两侧的两个相邻值为

$$Y_{188} = 0.9698581560 = 96.9858\%,$$

$$Y_{189} = 0.9700176367 = 97.0018\%.$$

总收率随循环次数增加而增大，因此最少需要

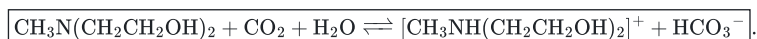
$$\boxed{189 \text{ 个循环，共计}}.$$

由于第一个循环的收率为 15.0%，这意味着在第一个循环之后再行 188 个循环。每个循环都会加入新鲜反应物；若按仅对最初加入的一份原料反复循环来计算，描述的将是另一种体系。

## 7.4 — 二氧化碳的吸收

化合物 **3** 为 **N-甲基二乙醇胺**，SMILES 为 CN(CCO)CCO。

它是一种叔胺。在水溶液中，溶解的二氧化碳形成碳酸氢根离子，同时该胺接受一个质子：



产物为 **N-甲基二乙醇铵离子**，SMILES 为 C[NH+](CCO)CCO，以及 **碳酸氢根离子（重碳酸根离子）**，SMILES 为 O=C([O-])O。

该胺最初没有与氮相连的氢，因此相应的净吸收产物为碳酸氢根离子，而不是普通的胺基甲酸盐。

## 7.5 — 配合物 5 的结构

将中性钳形配体记为  $L$ 。其名称为 **2,6-双[(二叔丁基膦基)甲基]吡啶**，SMILES 为：

n1c(CP(C(C)(C)C)C(C)(C)C)cccc1CP(C(C)(C)C)C(C)(C)C

它通过两个磷原子和吡啶氮原子配位，形成经式  $\kappa^3\text{-P,N,P}$  排列。

起始配合物 **4** 为 **三氯(L)合钼(III)**，[MoCl3(L)]。使用配位键的 SMILES 表示为：

[Cl-]->[Mo+3]12(-[Cl-])(-[Cl-])<-n3c(CP->1(C(C)(C)C)C(C)(C)C)cccc3CP->2(C(C)(C)C)C(C)(C)C

**4** 的物质的量为

$$n(4) = \frac{1.00 \text{ g}}{597.824 \text{ g mol}^{-1}} = 1.672733 \times 10^{-3} \text{ mol}.$$

对于氮气，

$$n(\text{N}_2) = \frac{PV}{RT} = \frac{(1.0 \times 10^5 \text{ Pa})(94.97 \times 10^{-6} \text{ m}^3)}{(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(273.15 \text{ K})} = 4.181915 \times 10^{-3} \text{ mol}.$$

因此，

$$\frac{n(\text{N}_2)}{n(4)} = 2.50005 \approx \frac{5}{2}.$$

因此，最简单的产物单元含有 **两个钼原子和五个氮分子**。

三个当量的钠将每个钼(III)中心还原为钼(0)，并使三个氯离子以氯化钠的形式脱去。配平后的制备反应为



氯化钠的化学式单位 SMILES 为 [Na+].[Cl-]；汞作为形成汞齐的介质。

预期结构为  $\mu\text{-双氮-双}[(\text{双氮})(L)\text{合钼}(0)]$ ：

- 画出两个钼中心，以一个线性、两端均为端接配位的  $\text{Mo-N}\equiv\text{N-Mo}$  桥相连。
- 在每个钼上连接一个三齿 PNP 配体。
- 在每个钼上再连接两个以端接方式配位的端位双氮配体。
- 每个钼中心近似为八面体构型。两个端位双氮配体互为反式；桥联双氮与吡啶氮互为反式。

这样，每个金属中心均满足 18 电子构型：

$$6 \quad (d^6 \text{ Mo}(0)) + 6 \quad (L) + 4 \quad (\text{两个端位双氮配体}) + 2 \quad (\text{桥联双氮配体}) = 18.$$

使用配位键明确表示这一连接关系的 SMILES 为：

[Mo]12(-N#N)(-N#N)(-N#N->[Mo]45(-N#N)(-N#N)<-n6c(CP->4(C(C)(C)C)C(C)(C)C)cccc6CP->5(C(C)(C)C)C(C)(C)C->1(C(C)(C)C)C(C)(C)C)cccc3CP->2(C(C)(C)C)C(C)(C)C

该 SMILES 指定了给体原子与金属之间的连接关系；八面体构型和反式关系由上述绘图说明给出。

## 7.6 — 还原剂/添加剂组合的排序

比较所给实验表中的组合 1 和 4 可知，电势更负、还原性更强的还原剂有利于生成氨。组合 A 的电势为  $-0.09 \text{ V}$ ，负值的绝对值小得多，因此预计其收率最低。

B、C 和 D 的还原剂电势相同，抗衡离子也相同。比较实验组合 3 和 4 可见，添加剂的  $pK_a$  越高，即酸性越弱，氨收率越高。应用这一趋势可得

$$pK_a(\text{B}) = 15.0 > pK_a(\text{C}) = 13.7 > pK_a(\text{D}) = 10.6.$$

因此，题目所要求的收率递减顺序为

$$\boxed{\text{B} > \text{C} > \text{D} > \text{A}}.$$

## 7.7 — 氮化物及化合物 10 的鉴定

对于二元氮化物  $\text{E}_a\text{N}_b$ ，设元素  $E$  的氧化态为  $+z$ 。由于氮以氮化物离子的形式存在，

$$az = 3b.$$

其氮的质量分数为

$$w(\text{N}) = \frac{14.01b}{aM(E) + 14.01b}.$$

利用  $a/b = 3/z$ ，

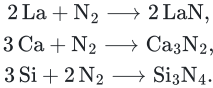
$$\frac{M(E)}{z} = \frac{14.01}{3} \left( \frac{1}{w(\text{N})} - 1 \right).$$

由所给的三个百分数可作出如下鉴定：

| 化合物 | $M(E)/z, \text{ g mol}^{-1}$ | 鉴定结果                             | 化学式                            | 计算得到的氮质量分数 |
|-----|------------------------------|----------------------------------|--------------------------------|------------|
| 7   | 46.3125                      | $z = 3, M(E) \approx 138.94$ : 镧 | LaN                            | 9.1623%    |
| 8   | 20.0390                      | $z = 2, M(E) \approx 40.078$ : 钙 | Ca <sub>3</sub> N <sub>2</sub> | 18.8992%   |
| 9   | 7.02254                      | $z = 4, M(E) \approx 28.090$ : 硅 | Si <sub>3</sub> N <sub>4</sub> | 39.9401%   |

因此，**7** 为**氮化镧(III)**，化学式单位 SMILES 为 [La+3].[N-3]；**8** 为**氮化钙**，化学式单位 SMILES 为 [Ca+2].[Ca+2].[Ca+2].[N-3].[N-3]；**9** 为**氮化硅**。后者以形式电荷分离方式表示的组成为 [Si+4].[Si+4].[Si+4].[N-3].[N-3].[N-3].[N-3]。这些不相连的字符串表示的是组成，而不是晶体中的连接关系；氮化硅是一种具有延展共价网络的固体。

它们由单质生成的反应可表示为



为求出 **10** 的组成，将给定的质量比换算为物质的量比：

$$\begin{aligned} M(\text{LaN}) &= 152.91 \text{ g mol}^{-1}, \\ M(\text{Ca}_3\text{N}_2) &= 148.26 \text{ g mol}^{-1}, \\ M(\text{Si}_3\text{N}_4) &= 140.31 \text{ g mol}^{-1}, \quad M(\text{SiO}_2) = 60.09 \text{ g mol}^{-1}. \end{aligned}$$

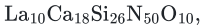
因此

$$n(\text{LaN}) : n(\text{Ca}_3\text{N}_2) : n(\text{Si}_3\text{N}_4) : n(\text{SiO}_2) = \frac{5.09}{152.91} : \frac{2.96}{148.26} : \frac{3.27}{140.31} : \frac{1.00}{60.09}.$$

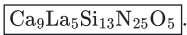
归一化后得到

$$2.00025 : 1.19969 : 1.40043 : 1 \approx 10 : 6 : 7 : 5.$$

这些物质的量对应的总组成为

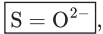


约简后得到实验式



题目规定的结构式中已含有 Si<sub>12</sub>N<sub>24</sub>。扣除这一单元后，除金属阳离子外，还剩下一个硅原子、一个氮原子和五个氧原子。

因此，两个相同的单原子阴离子必定为氧离子：



名称为**氧离子**，SMILES 为 [O-2]。

将两个氧原子分配给这两个氧离子后，四面体阴离子的组成为 SiNO<sub>3</sub>。其电荷为

$$(+4) + (-3) + 3(-2) = -5,$$

因此



这就是一**氮三氧合硅酸根(5-)**，SMILES 为 [N-2][Si]([O-])([O-])[O-]。绘图时，将硅置于四面体中心，与一个氮原子和三个氧原子成键。该含键 SMILES 中的形式电荷之和为  $-5$ ；氮的氧化态仍为  $-3$ 。

因此，**10** 是一种**氧氮硅酸钙镧**，其化学式为

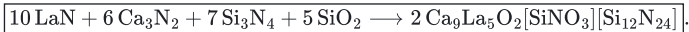


一种指派方式为  $Q = \text{Ca}^{2+}$ 、 $\alpha = 9$ 、 $R = \text{La}^{3+}$  和  $\beta = 5$ 。两种阳离子的 SMILES 分别为 [Ca+2] 和 [La+3]。

电荷平衡验证了这一结果：

$$\begin{aligned} 9(2) + 5(3) &= 33, \\ 2(-2) + (-5) + [12(4) + 24(-3)] &= -4 - 5 - 24 = -33. \end{aligned}$$

配平后的合成反应为



题目未给出延展的 [Si<sub>12</sub>N<sub>24</sub>]<sup>24-</sup> 骨架的连接关系，因此无法仅由化合物 **10** 的化学式推断出其完整晶体的唯一结构 SMILES。

解答已与官方解答核对。

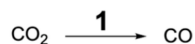
## 题目 8：二氧化碳的循环利用

### T8. 二氧化碳的循环利用

7%

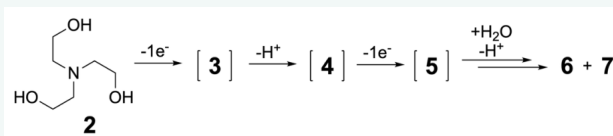
| 8.1 | 8.2 | 8.3 | 8.4 | 8.5 | 8.6 | 8.7 | 8.8 | 8.9 | 8.10 | Σ  |
|-----|-----|-----|-----|-----|-----|-----|-----|-----|------|----|
| 2   | 16  | 2   | 29  | 5   | 10  | 2   | 4   | 12  | 2    | 84 |

从大气中去除 CO<sub>2</sub> 气体是应对气候变化的关键。一种很有前景的方法是利用分子催化剂 **1**，通过光催化将 CO<sub>2</sub> 还原为 CO。



8.1 写出酸性介质中  $\text{CO}_2$  还原为  $\text{CO}$  的半反应方程式。2.0 分

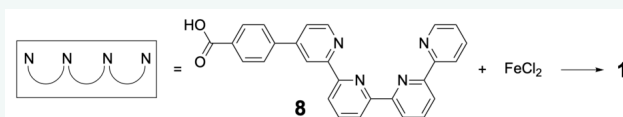
与之配对的氧化反应由牺牲性还原剂 **2** 在水溶液中按以下机理进行：



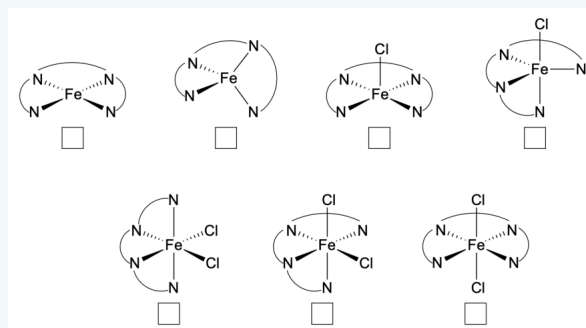
物种 **3**、**4** 和 **5** 是寿命很短的离子和/或自由基中间体。**7** 在  $[\text{Ag}(\text{NH}_3)_2]\text{OH}$  检验中产生银镜。

8.2 画出 **3-7** 的结构。16.0 分

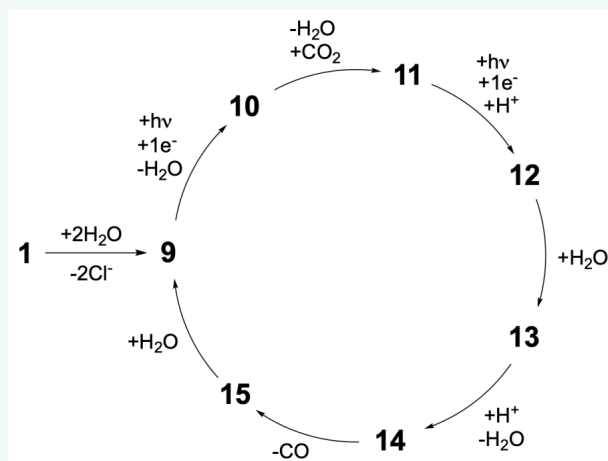
催化剂 **1** 可通过以下反应合成。



8.3 勾选 **1** 的正确几何构型。2.0 分



将 **1** 负载于晶态氮化碳 ( $\text{C}_3\text{N}_4$ ) 载体材料上后，它可通过以下机理还原  $\text{CO}_2$ 。



8.4 画出 **9-15** 的结构。使用上图中配体 **8** 的示意结构。对于 **9-15**，注明 Fe 的氧化态 *OS*、配位数 *CN* 和价电子数 *VE*，以及相应配合物结构的总电荷 *Z*。注意：答题纸上已给出部分信息。29.0 分

**9**

$Z = \underline{\hspace{1cm}}$

$OS = \underline{\hspace{1cm}} \quad CN = \underline{\hspace{1cm}} \quad VE = \underline{\hspace{1cm}}$

**10**

$Z = \underline{\hspace{1cm}}$

$OS = \underline{\hspace{1cm}} \quad CN = \underline{\hspace{1cm}} \quad VE = \underline{\hspace{1cm}}$

**11**

$Z = \underline{\hspace{1cm}}$

$OS = +3 \quad CN = 6 \quad VE = \underline{\hspace{1cm}}$

**12**

$Z = \underline{\hspace{1cm}}$

$OS = \underline{\hspace{1cm}} \quad CN = 5 \quad VE = \underline{\hspace{1cm}}$

13

 $Z = \underline{\hspace{2cm}}$  $OS = +2 \quad CN = \underline{\hspace{2cm}} \quad VE = \underline{\hspace{2cm}}$ 

14

 $Z = \underline{\hspace{2cm}}$  $OS = \underline{\hspace{2cm}} \quad CN = \underline{\hspace{2cm}} \quad VE = \underline{\hspace{2cm}}$ 

15

 $Z = \underline{\hspace{2cm}}$  $OS = \underline{\hspace{2cm}} \quad CN = \underline{\hspace{2cm}} \quad VE = 16$ 

8.5 已知催化剂的质量分数  $\omega_{\text{cat}} = 3.8\%$ ,  $\text{C}_3\text{N}_4$  的比表面积为  $17.8 \text{ m}^2 \text{ g}^{-1}$ , 计算负载 1 的  $\text{C}_3\text{N}_4$  每  $\text{nm}^2$  上的催化剂分子数  $N_{\text{cat}}$ 。  
 $M_{\text{cat}} = 557.21 \text{ g mol}^{-1}$ 。5.0 分

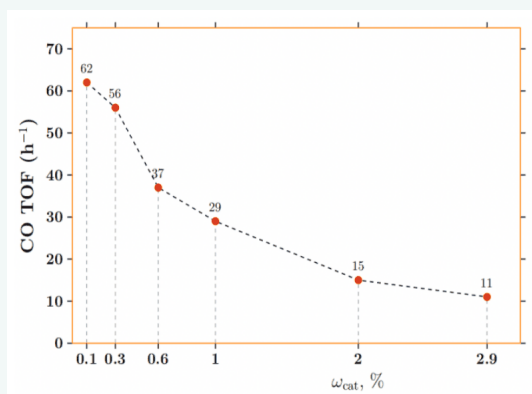
催化剂的转换频率 (TOF) 是每个活性催化剂分子每小时生成的产物分子数。在功率为 50 mW 的 LED 光照 ( $\lambda = 390 \text{ nm}$ ) 下, 对于负载了 1、且  $\omega_{\text{cat}} = 3.8\%$  的 10 mg  $\text{C}_3\text{N}_4$ , TOF 为  $8 \text{ h}^{-1}$ 。

量子产率的计算公式如下:

$$\varphi = \frac{\text{参与反应的电子数}}{\text{入射光子数}} \cdot 100\%$$

8.6 计算生成 CO 的量子产率  $\varphi(\%)$ 。10.0 分

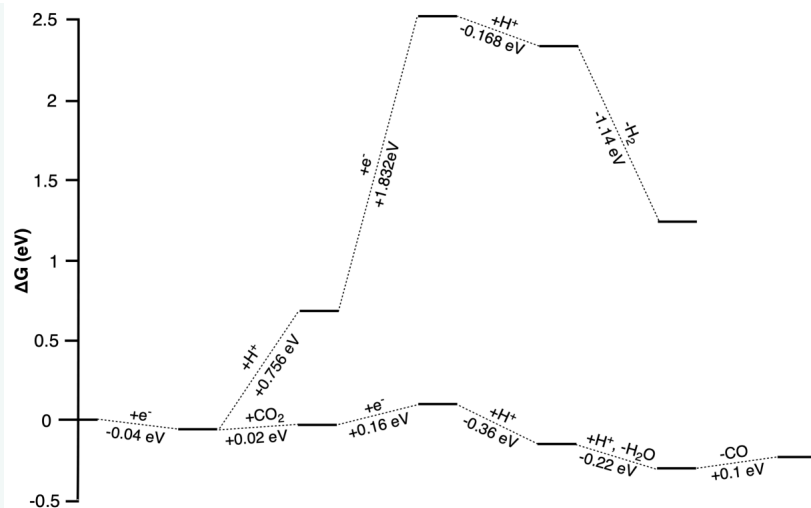
下图展示了 CO 的 TOF 随  $\omega_{\text{cat}}$  的变化。



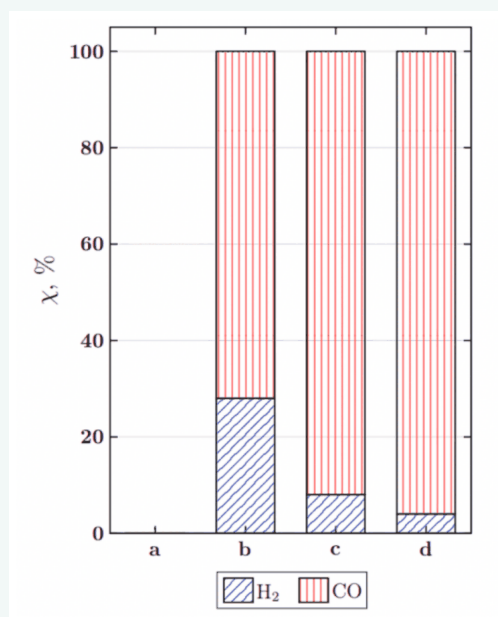
8.7 在  $0.1 \leq \omega_{\text{cat}} \leq 2.9$  范围内, 随着  $\omega_{\text{cat}}$  增大, 每克负载 1 的  $\text{C}_3\text{N}_4$  生成 CO 的总速率如何变化? 勾选正确选项。2.0 分

- a) 增大
- b) 减小
- c) 不变

$\text{CO}_2$  的还原可能伴随额外质子的还原。下图展示了这两个反应过程中的吉布斯能变化。



用不同的 LED 照射该体系。下图展示了四种不同条件下还原  $\text{CO}_2$  时生成的  $\text{H}_2$  和  $\text{CO}$  的摩尔百分数  $\chi$ ：无光照 (N)，以及红光 (R)、绿光 (G) 和蓝光 (B) 照射。

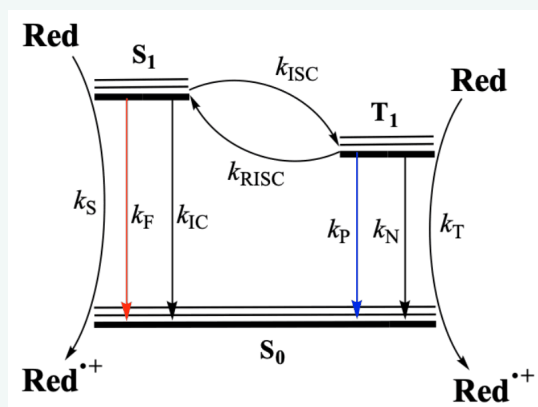


8.8 勾选上述四种条件中分别对应图中 a、b、c 和 d 的条件。4.0 分

与  $\text{C}_3\text{N}_4$  相比，光敏剂 (PS) 在还原  $\text{CO}_2$  方面具有一些优势。含  $\text{Mn}(\text{II})$  的配合物与 PS 联用可实现约 23% 的量子产率。在该体系中，还原剂 (Red) 对 PS 的单重态 ( $\text{S}_1$ ) 和三重态 ( $\text{T}_1$ ) 激发态进行还原性猝灭，形成  $\text{PS}^{\bullet-}$ ，后者通过含  $\text{Mn}(\text{II})$  的配合物向  $\text{CO}_2$  提供电子。



下列雅布隆斯基图描述了 PS 中发生的过程：



$\tau_0(\text{S}_1) = 2.9 \text{ ns}$  且  $\tau_0(\text{T}_1) = 84 \text{ }\mu\text{s}$ , 其中  $\tau_0$  是不存在猝灭剂时的发光寿命。

8.9 当  $[\text{Red}] = 0.1 \text{ M}$  时, 计算  $\text{S}_1$  和  $\text{T}_1$  态的猝灭百分比  $\eta_q$  (以 % 表示)。注意: 此处  $k_{\text{ISC}}$  和  $k_{\text{RISC}}$  的数值可忽略不计。12.0 分

8.10 当  $[\text{Red}]$  增大时,  $\text{S}_1$  和  $\text{T}_1$  态的发光寿命如何变化?

勾选正确选项。2.0 分

- a) 增大  
b) 减小  
c) 不变

物理常数与方程

常数

| 常数           | 数值                                               |
|--------------|--------------------------------------------------|
| 阿伏伽德罗常数      | $N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$    |
| 摩尔气体常数       | $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$    |
| 法拉第常数        | $F = 96485 \text{ C mol}^{-1}$                   |
| 普朗克常数        | $h = 6.626 \times 10^{-34} \text{ J s}$          |
| 真空中的光速       | $c = 2.998 \times 10^8 \text{ m s}^{-1}$         |
| 电子质量         | $m_e = 9.109 \times 10^{-31} \text{ kg}$         |
| 电子电荷量        | $e = 1.602 \times 10^{-19} \text{ C}$            |
| 标准压力         | $P^\circ = 1 \text{ bar} = 10^5 \text{ Pa}$      |
| 25 °C 时水的离子积 | $K_w = 1.00 \times 10^{-14}$                     |
| 摄氏温标的零点      | $0^\circ\text{C} = 273.15 \text{ K}$             |
| 电子伏特         | $1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}$ |
| 瓦特           | $1 \text{ W} = 1 \text{ J s}^{-1}$               |
| 库仑           | $1 \text{ C} = 1 \text{ A s}$                    |
| 纳米           | $1 \text{ nm} = 1 \times 10^{-9} \text{ m}$      |
| 埃            | $1 \text{ \AA} = 1 \times 10^{-10} \text{ m}$    |
| 公吨           | $1 \text{ ton} = 1000 \text{ kg}$                |
| 升            | $1 \text{ L} = 1 \text{ dm}^3$                   |

方程

| 方程                                                                                    | 表达式                                                                         |
|---------------------------------------------------------------------------------------|-----------------------------------------------------------------------------|
| 理想气体状态方程                                                                              | $PV = nRT$                                                                  |
| 道尔顿定律                                                                                 | $P_i = x_i P$                                                               |
| 比尔-朗伯定律                                                                               | $A = \log_{10} \frac{I_0}{I} = \varepsilon cl$                              |
| 光子的能量                                                                                 | $E = h\nu = \frac{hc}{\lambda}$                                             |
| 热量与温度变化                                                                               | $Q = nC_m \Delta T$                                                         |
| 吉布斯能的定义                                                                               | $G = H - TS$                                                                |
| 吉布斯能与平衡常数                                                                             | $\Delta_r G^\circ = -RT \ln K$                                              |
| 焓变随温度的变化 (当 $\Delta_r C_p = \text{const}$ 时)                                          | $\Delta_r H_{T_2} = \Delta_r H_{T_1} + \Delta_r C_p (T_2 - T_1)$            |
| 熵变随温度的变化 (当 $\Delta_r C_p = \text{const}$ 时)                                          | $\Delta_r S_{T_2} = \Delta_r S_{T_1} + \Delta_r C_p \ln \frac{T_2}{T_1}$    |
| 亨德森-哈塞尔巴尔赫方程                                                                          | $\text{pH} = \text{p}K_a + \log_{10} \frac{[\text{A}^-]}{[\text{HA}]}$      |
| 平均反应速率                                                                                | $r = \frac{\Delta c}{\Delta t}$                                             |
| 速率方程                                                                                  | $r = k[\text{A}]^x [\text{B}]^y$                                            |
| 阿伦尼乌斯定律                                                                               | $k = A \exp \left( -\frac{E_a}{RT} \right)$                                 |
| 一级反应的积分速率方程                                                                           | $c = c_0 e^{-kt}, \quad kt = \ln \frac{c_0}{c}$                             |
| 一级反应中反应物的寿命                                                                           | $\tau = \frac{1}{k}$                                                        |
| n 级反应的积分速率方程 ( $n \neq 1$ )                                                           | $kt = \frac{1}{n-1} (c^{1-n} - c_0^{1-n}), \quad \text{适用于 } n \neq 1$      |
| 连续反应中间体的浓度: $\text{A} \xrightarrow{k_1} \text{B} \xrightarrow{k_2} \text{D}$          | $[\text{B}] = \frac{k_1 [\text{A}]_0}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t})$ |
| 竞争反应的产物之比: $\text{A} \xrightarrow{k_1} \text{B}, \text{A} \xrightarrow{k_2} \text{C}$ | $\frac{[\text{B}]}{[\text{C}]} = \frac{k_1}{k_2}$                           |
| 米氏方程                                                                                  | $r_0 = r_{\max} \frac{[\text{S}]_0}{K_M + [\text{S}]_0}$                    |

| 方程                       | 表达式                                                    |
|--------------------------|--------------------------------------------------------|
| 比表面积                     | $s = \frac{S}{m}$                                      |
| 数列：等差数列、等比数列             | $a_n = a_1 + d(n-1), a_n = a_1 q^{n-1}$                |
| 等比数列求和                   | $\sum_{k=0}^n a_1 q^k = a_1 \frac{q^{n+1} - 1}{q - 1}$ |
| 半径为 $r$ 的球的体积            | $V = \frac{4}{3} \pi r^3$                              |
| 半径为 $r$ 的球的表面积           | $S = 4 \pi r^2$                                        |
| 底面半径为 $r$ 、高为 $h$ 的圆锥的体积 | $V = \frac{1}{3} \pi r^2 h$                            |
| 底面半径为 $r$ 、高为 $h$ 的圆柱的体积 | $V = \pi r^2 h$                                        |

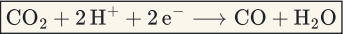
将所有气体视为理想气体。

在平衡常数计算中，所有浓度均以  $1 \text{ mol dm}^{-3}$  的浓度为参照。

题目译自官方英文原文。

答案

- 8.1.



- 8.2.

| 物种 | 物种说明                      | SMILES                          |
|----|---------------------------|---------------------------------|
| 3  | 三乙醇胺自由基阳离子；自由基和正电荷均位于氮原子上 | <chem>[N+](CCO)(CCO)CCO</chem>  |
| 4  | 由三乙醇胺衍生的 $\alpha$ -氨基碳自由基 | <chem>OCCN(CCO)[CH]CO</chem>    |
| 5  | N,N-双(2-羟乙基)-2-羟基乙亚胺鎓离子   | <chem>[N+](CCO)(CCO)=CCO</chem> |
| 6  | 二乙醇胺                      | <chem>OCCNCCO</chem>            |
| 7  | 羟基乙醛，即 2-羟基乙醛             | <chem>OCC=O</chem>              |

- 8.3. 勾选右下角的第七个结构：八面体构型的反式-二氯(L)合铁(II)，四个氮给体位于赤道平面内，两个氯配体互为反式。这里  $L$  为配体 8。
- 8.4. 中性配体  $L$  的四个氮原子始终全部参与配位。完整的配位 SMILES 和绘图说明见解答。

| 物种 | 结构与配位方式                                                                             | $OS$ | $CN$ | $VE$ | $Z$ |
|----|-------------------------------------------------------------------------------------|------|------|------|-----|
| 9  | $[\text{Fe}(\text{L})(\text{H}_2\text{O})_2]^{2+}$                                  | +2   | 6    | 18   | +2  |
| 10 | $[\text{Fe}(\text{L})(\text{H}_2\text{O})]^+$                                       | +1   | 5    | 17   | +1  |
| 11 | $[\text{Fe}(\text{L})(\text{CO}_2)]^+$ ；以 C、O 双齿配位的 $\text{CO}_2^{2-}$ ，形成 Fe—C—O 环 | +3   | 6    | 17   | +1  |
| 12 | $[\text{Fe}(\text{L})(\text{COOH})]^+$ ；通过碳原子配位的羟基羰基                                | +2   | 5    | 16   | +1  |
| 13 | $[\text{Fe}(\text{L})(\text{COOH})(\text{H}_2\text{O})]^+$ ；通过碳原子配位的羟基羰基            | +2   | 6    | 18   | +1  |
| 14 | $[\text{Fe}(\text{L})(\text{CO})(\text{H}_2\text{O})]^{2+}$ ；通过碳原子配位的羰基             | +2   | 6    | 18   | +2  |
| 15 | $[\text{Fe}(\text{L})(\text{H}_2\text{O})]^{2+}$                                    | +2   | 5    | 16   | +2  |

- 8.5.  $N_{\text{cat}} \approx 2.40 \text{ 个分子 nm}^{-2}$ ，此处将 3.8% 视为催化剂在复合材料中的质量分数，将  $17.8 \text{ m}^2 \text{ g}^{-1}$  视为每克未负载载体的表面积。如果该表面积是按每克负载材料计，则结果为  $2.31 \text{ 个分子 nm}^{-2}$ 。
- 8.6. 对于 10 mg 未负载载体， $\varphi \approx 1.93\%$ 。如果 10 mg 指负载材料的总质量，则  $\varphi \approx 1.86\%$ 。两者均约为 1.9%。
- 8.7. a) 增大。
- 8.8.  $a = \text{N}, \quad b = \text{B}, \quad c = \text{G}, \quad d = \text{R}$ 。
- 8.9.

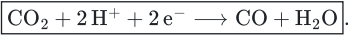
$$\eta_q(\text{S}_1) = 43.9\%, \quad \eta_q(\text{T}_1) = 99.92\%$$

- 8.10. 两个态均为 b) 减小。

解答

8.1 — 还原半反应方程式

碳的氧化态由二氧化碳中的 +4 变为一氧化碳中的 +2，因此需要两个电子。用水配平氧原子，用质子配平氢原子，得到



原子数和电荷均已配平。

本解答中使用的小分子物种包括二氧化碳  $\text{O}=\text{C}=\text{O}$ 、一氧化碳  $[\text{C-}]\#[\text{O+}]$ 、水  $\text{O}$ 、氢气  $[\text{H}][\text{H}]$ 、质子  $[\text{H+}]$  和氯离子  $[\text{Cl-}]$ 。

## 8.2 — 牺牲性还原剂的氧化

化合物 **2** 为三乙醇胺,  $\text{OCCN}(\text{CCO})\text{CCO}$ 。用  $R$  表示 2-羟乙基  $-\text{CH}_2\text{CH}_2\text{OH}$ , 则 **2** 可表示为  $\text{R}_3\text{N}$ 。

第一次氧化从氮原子的孤电子对中移去一个电子:



因此, **3** 是答案中给出的以氮为中心的自由基阳离子。

去质子化发生在与氮原子直接相连的碳原子上。三个支链均等价, 因此任选其中一个, 均得到相同构造的中间体:



由此生成 **4**, 其未成对电子位于  $\alpha$ -碳原子上。再失去一个电子, 得到亚胺鎓离子 **5**:



水进攻具有亲电性的亚胺鎓碳原子。经质子转移及该碳-氮键断裂, 生成仲胺 **6** 和醛 **7**:



因此, **6** 为二乙醇胺, **7** 为羟基乙醛。**7** 中的醛基使其银镜检验呈阳性。

总氧化半反应方程式为



绘制所要求的结构时, 应在 **3** 中标出氮自由基阳离子, 在 **4** 中标出  $\alpha$ -碳自由基, 在 **5** 中标出带正电荷的氮-碳双键。答案中的 SMILES 指定了它们的连接关系和自由基位置。

## 8.3 — 催化剂 **1** 的几何构型

配体 **8** 记为  $L$ , 是 4-(4-羧基苯基)-2,2':6',2''-四联吡啶。其 SMILES 为

O=C(O)c1ccc(-c2ccnc(-c3cccc(-c4cccc(-c5ccccc5)n4)n3)c2)cc1

其四个吡啶氮原子提供四个中性给体位点。加上两个氯配体, 铁的配位数为六。四联吡啶的给体排列使四个氮原子分布于赤道平面内, 留下两个轴向位点供互为反式的氯配体占据。

因此, **1** 为反式-二氯(L)合铁(II), 正确选项是右下角的结构。

配位 SMILES:

[Cl-]->[Fe+2]6789<-[Cl-].O=C(O)c1ccc(-c2ccn->6c(-c3cccc(-c4cccc(-c5ccccc5->7)n4->8)n3->9)c2)cc1

这里及下文使用的配位 SMILES 以  $\rightarrow$  和  $\leftarrow$  表示配位键。相同的环编号将点号两侧的配体与铁连接起来。这些字符串指定连接关系和形式电荷; 配位几何构型则用文字说明。

## 8.4 — 催化中间体与电子计数

$L$  的侧链羧基保持不变, 因此  $L$  为中性, 并提供  $4 \times 2 = 8$  个电子。

铁是第 8 族金属, 因此

$$d\text{电子数} = 8 - OS.$$

采用离子法计数时, 每个配位水、羧基、氮给体或 X 型给体均贡献两个电子。

## 9 — 二水(L)合铁(II)离子

**1** 的两个氯配体均被水取代:



在铁周围画出四个氮给体, 并在原来氯离子占据的位置画出两个水配体。

SMILES:

[OH2]->[Fe+2]6789<-[OH2].O=C(O)c1ccc(-c2ccn->6c(-c3cccc(-c4cccc(-c5ccccc5->7)n4->8)n3->9)c2)cc1

所有配体均为中性, 因此  $Z = OS = +2$ 。电子数为

$$VE = 6 + 8 + 2(2) = 18, \quad CN = 6.$$

## 10 — 水(L)合铁(I)离子

**9** 经单电子还原, 同时失去一个水配体, 生成 **10**:



画出四个氮给体和一个水配体。

SMILES:

[OH2]->[Fe+]6789.O=C(O)c1ccc(-c2ccn->6c(-c3cccc(-c4cccc(-c5ccccc5->7)n4->8)n3->9)c2)cc1

因此

$$OS = +1, \quad Z = +1, \quad CN = 5, \quad VE = 7 + 8 + 2 = 17.$$

## 11 — 以 C、O 配位的亚碳酸根合铁(III)配合物

剩余的水被二氧化碳取代。答题纸给出的信息指定  $OS = +3$  且  $CN = 6$ 。由于  $L$  提供四个配位位点, 二氧化碳必须通过两个原子配位。

画出一个  $\text{Fe}-\text{C}-\text{O}$  三元环, 其中碳原子还与第二个氧原子形成双键。这是通过 C、O 配位、形式上经双电子还原的二氧化碳配体  $\text{CO}_2^{2-}$ , 通常称为亚碳酸根。

SMILES:

[Fe+3]16789<-[O-][C-](=O)->1.O=C(O)c1ccc(-c2ccn->6c(-c3cccc(-c4cccc(-c5ccccc5->7)n4->8)n3->9)c2)cc1

该配体的形成在形式上使两个电子从铁(Ⅰ)转移至二氧化碳,得到铁(Ⅲ)。因此,

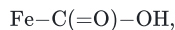
$$Z = (+3) + (-2) = +1,$$

$$CN = 4 + 2 = 6, \quad VE = 5 + 8 + 4 = 17.$$

## 12 — 羟基羰基(L)合铁(Ⅱ)离子

加入一个电子使铁(Ⅲ)还原为铁(Ⅱ)。配位氧原子发生质子化,使 Fe—C—O 环打开,留下通过碳原子配位的羟基羰基配体。

画出如下连接关系



其中四个氮给体仍全部与铁相连,且没有水配体。

SMILES:

[Fe+2]6789<-[C-](=O)O.O=C(O)c1ccc(-c2ccn->6c(-c3cccc(-c4cccc(-c5ccccc5->7)n4->8)n3->9)c2)cc1

羟基羰基配体的形式电荷为 -1, 因此

$$OS = +2, \quad Z = +1, \quad CN = 5, \quad VE = 6 + 8 + 2 = 16.$$

## 13 — 水(羟基羰基)(L)合铁(Ⅱ)离子

水与 12 配位:



画出相同的通过碳原子配位的羟基羰基,并增加一个水配体。

SMILES:

[OH2]->[Fe+2]6789<-[C-](=O)O.O=C(O)c1ccc(-c2ccn->6c(-c3cccc(-c4cccc(-c5ccccc5->7)n4->8)n3->9)c2)cc1

水的配位既不改变电荷,也不改变氧化态:

$$OS = +2, \quad Z = +1, \quad CN = 6, \quad VE = 6 + 8 + 2 + 2 = 18.$$

## 14 — 水(羰基)(L)合铁(Ⅱ)离子

羟基羰基的质子化使其能够脱去水,生成羰基配体:



画出通过碳原子连接的一氧化碳,以及保留的水配体。

SMILES:

[OH2]->[Fe+2]6789<-[C-]#[O+].O=C(O)c1ccc(-c2ccn->6c(-c3cccc(-c4cccc(-c5ccccc5->7)n4->8)n3->9)c2)cc1

一氧化碳是中性双电子给体。因此

$$OS = +2, \quad Z = +2, \quad CN = 6, \quad VE = 6 + 8 + 2 + 2 = 18.$$

## 15 — 水(L)合铁(Ⅱ)离子

一氧化碳解离:



画出与四个氮给体和一个水配体配位的铁。

SMILES:

[OH2]->[Fe+2]6789.O=C(O)c1ccc(-c2ccn->6c(-c3cccc(-c4cccc(-c5ccccc5->7)n4->8)n3->9)c2)cc1

因此

$$OS = +2, \quad Z = +2, \quad CN = 5, \quad VE = 6 + 8 + 2 = 16,$$

这与给定的电子数一致。加入水后再生 9。

将循环中的各步相加,得到 8.1 中的还原半反应方程式。

## 8.5 — 催化剂分子的表面密度

采用质量分数的标准定义:

$$w = \omega_{\text{cat}} = \frac{m_{\text{cat}}}{m_{\text{cat}} + m_{\text{support}}} = 0.038.$$

取 1.000 g 负载材料,则有

$$m_{\text{cat}} = 0.038 \text{ g}, \quad m_{\text{support}} = 0.962 \text{ g}.$$

催化剂分子数为

$$N = \frac{0.038 \text{ g}}{557.21 \text{ g mol}^{-1}} (6.022 \times 10^{23} \text{ mol}^{-1}) = 4.1068 \times 10^{19}.$$

如果所给比表面积是按每克未负载的 C<sub>3</sub>N<sub>4</sub> 计,则其表面积为

$$S = (0.962 \text{ g})(17.8 \text{ m}^2 \text{ g}^{-1}) = 17.1236 \text{ m}^2 = 1.71236 \times 10^{19} \text{ nm}^2.$$

因此

$$N_{\text{cat}} = \frac{w N_A}{(1 - w) M_{\text{cat}} s 10^{18}} = 2.398 \approx 2.4 \text{ 个分子 nm}^{-2}.$$

如果  $17.8 \text{ m}^2 \text{ g}^{-1}$  是每克负载材料的表面积，则不含因子  $1 - w$ ：

$$N_{\text{cat}} = \frac{w N_A}{M_{\text{cat}} s 10^{18}} = 2.307 \approx 2.3 \text{ 个分子 nm}^{-2}.$$

8.6 — 量子产率

生成每个一氧化碳分子需要两个电子。

首先将题目所给的  $10 \text{ mg}$  理解为未负载载体的质量。此时催化剂的质量为

$$m_{\text{cat}} = \frac{w}{1 - w} m_{\text{support}} = \frac{0.038}{0.962} (0.010 \text{ g}) = 3.9501 \times 10^{-4} \text{ g}.$$

因此，

$$n_{\text{cat}} = \frac{3.9501 \times 10^{-4}}{557.21} = 7.0891 \times 10^{-7} \text{ mol}.$$

一小时内，

$$n_{\text{CO}} = (8 \text{ h}^{-1})(7.0891 \times 10^{-7} \text{ mol})(1 \text{ h}) = 5.6713 \times 10^{-6} \text{ mol}.$$

参与反应的电子数为

$$N_e = 2 n_{\text{CO}} N_A = 6.8305 \times 10^{18}.$$

每个入射光子的能量为

$$E_{\gamma} = \frac{hc}{\lambda} = \frac{(6.626 \times 10^{-34} \text{ J s})(2.998 \times 10^8 \text{ m s}^{-1})}{390 \times 10^{-9} \text{ m}} = 5.0935 \times 10^{-19} \text{ J}.$$

一小时内的入射能量为

$$Pt = (0.050 \text{ J s}^{-1})(3600 \text{ s}) = 180 \text{ J},$$

所以

$$N_{\gamma} = \frac{180}{5.0935 \times 10^{-19}} = 3.5339 \times 10^{20}.$$

因此

$$\varphi = \frac{6.8305 \times 10^{18}}{3.5339 \times 10^{20}} \times 100\% = 1.93\%.$$

如果  $10 \text{ mg}$  指负载材料的总质量，则

$$m_{\text{cat}} = (0.038)(0.010 \text{ g}) = 3.80 \times 10^{-4} \text{ g},$$

采用相同计算方法，得到

$$\varphi = 1.86\%.$$

无论采用哪种理解，结果均约为  $1.9\%$ 。

8.7 — 总速率与催化剂负载量的关系

TOF 是每个催化剂分子的反应速率。每克负载材料中催化剂的量随其质量分数成比例增加，因此

$$r_{\text{CO}} = \frac{w}{M_{\text{cat}}} \text{ TOF}.$$

所以，决定总速率的是乘积  $w \text{ TOF}$ ，而非单独的 TOF。

| 催化剂负载量 | TOF / $\text{h}^{-1}$ | $w \text{ TOF}$ / $\text{h}^{-1}$ |
|--------|-----------------------|-----------------------------------|
| 0.1%   | 62                    | 0.062                             |
| 0.3%   | 56                    | 0.168                             |
| 0.6%   | 37                    | 0.222                             |
| 1.0%   | 29                    | 0.290                             |
| 2.0%   | 15                    | 0.300                             |
| 2.9%   | 11                    | 0.319                             |

该乘积在图示的整个范围内持续增大。若改为按未负载载体质量归一化，则会引入因子  $1/(1 - w)$ ，该因子也随之增大，不会改变结论。

a) 增大

8.8 — 光照条件的判定

空白位置 **a** 对应无光照条件 **N**。

光子能量满足

$$E_{\text{blue}} > E_{\text{green}} > E_{\text{red}},$$

因为  $E = hc/\lambda$ 。

析氢支路中使自由能升高的变化幅度显著更大，其中包括一个  $+1.832 \text{ eV}$  的步骤。按照本题预期的定性解释，能量更高的光照使这一竞争途径的贡献增大。

氢气的比例从 **b** 到 **c** 再到 **d** 依次降低，分别约为  $28\%$ 、 $8\%$  和  $4\%$ 。因此，

$$\mathbf{a} = \mathbf{N}, \quad \mathbf{b} = \mathbf{B}, \quad \mathbf{c} = \mathbf{G}, \quad \mathbf{d} = \mathbf{R}.$$

### 8.9 — 猝灭效率

忽略系间窜越和反向系间窜越时，每个激发态均有两类相互竞争的衰减过程：

- 本征衰减，总速率常数为  $k_0 = 1/\tau_0$ ；
- 还原性猝灭，准一级速率常数为  $k_q[\text{Red}]$ 。

因此，一个激发态分子被猝灭的概率为

$$\eta_q = \frac{k_q[\text{Red}]}{k_0 + k_q[\text{Red}]} \times 100\% = \frac{k_q[\text{Red}]\tau_0}{1 + k_q[\text{Red}]\tau_0} \times 100\%.$$

对于单重态，

$$k_S[\text{Red}]\tau_0(S_1) = (2.7 \times 10^9 \text{ M}^{-1}\text{s}^{-1})(0.1 \text{ M})(2.9 \times 10^{-9} \text{ s}) = 0.783.$$

因此

$$\eta_q(S_1) = \frac{0.783}{1 + 0.783} \times 100\% = 43.9\%.$$

对于三重态，

$$k_T[\text{Red}]\tau_0(T_1) = (1.5 \times 10^8 \text{ M}^{-1}\text{s}^{-1})(0.1 \text{ M})(84 \times 10^{-6} \text{ s}) = 1260.$$

因此

$$\eta_q(T_1) = \frac{1260}{1261} \times 100\% = 99.92\%.$$

虽然三重态的猝灭速率常数较小，但其未被猝灭时的寿命长得多，使猝灭几乎定量进行。

### 8.10 — 发光寿命与还原剂浓度的关系

观测到的寿命为

$$\tau = \frac{1}{k_0 + k_q[\text{Red}]} = \frac{\tau_0}{1 + k_q[\text{Red}]\tau_0}.$$

增大还原剂浓度会增大总衰减速率，因此两个激发态的寿命均缩短。

在 8.9 所用的浓度下，寿命为

$$\begin{aligned}\tau(S_1) &= \frac{2.9 \text{ ns}}{1.783} = 1.63 \text{ ns}, \\ \tau(T_1) &= \frac{84 \mu\text{s}}{1261} = 0.0666 \mu\text{s} = 66.6 \text{ ns}.\end{aligned}$$

因此，正确选项为

$$\text{b) 减小，两个态均如此}.$$

解答已与官方解答核对。

## 题目 9：环糊精化学

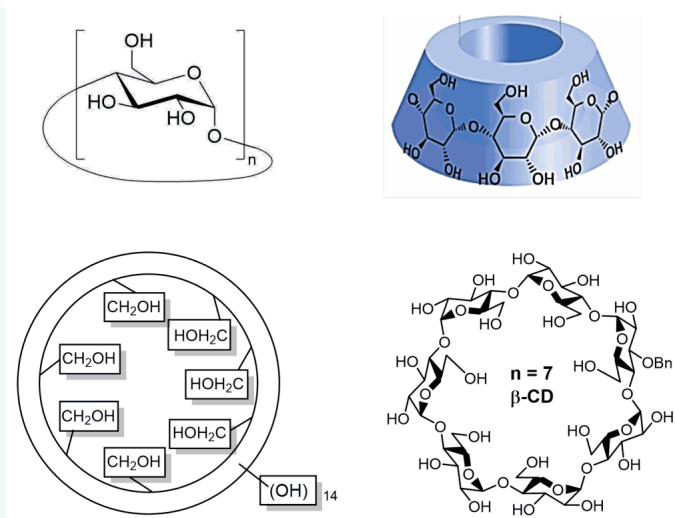
### T9. 环糊精化学

7%

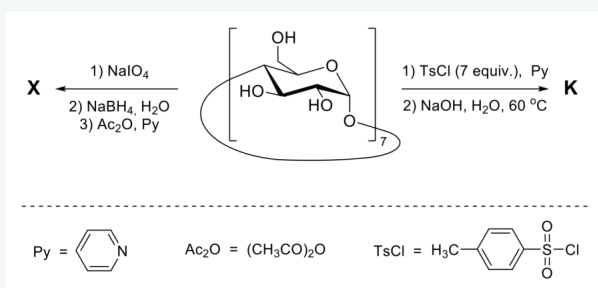
| 9.1 | 9.2 | 9.3 | 9.4 | 9.5 | 9.6 | 9.7 | 9.8 | 9.9 | $\Sigma$ |
|-----|-----|-----|-----|-----|-----|-----|-----|-----|----------|
| 2   | 6   | 8   | 3   | 2   | 4   | 6   | 18  | 4   | 53       |

环糊精 (CD) 是一类环状低聚糖，由葡萄糖亚基通过  $\alpha$ -1,4-糖苷键连接而成。最常见的三种环糊精 ( $\alpha$ -、 $\beta$ -、 $\gamma$ -环糊精) 分别含有 6、7 和 8 个  $\alpha$ -D-吡喃葡萄糖苷单元。

**9.1 计算  $\beta$ -CD 的摩尔质量。假设  $M_w(\text{葡萄糖}) = 180.16 \text{ g mol}^{-1}$ 。2.0 分**

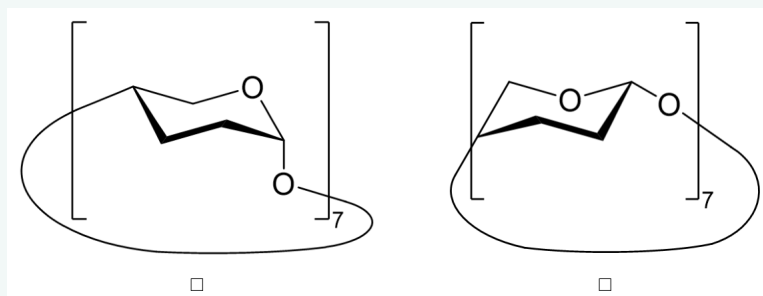


CD 兼具大环化合物的性质与葡萄糖的化学性质，这一点在 **X** 的合成中得到了体现。由于处于 CD 结构中，伯羟基和仲羟基表现出不同的反应活性。Stoddart 等人合成了化合物 **K**，其中每个吡喃葡萄糖苷单元仅保留一个游离 OH 基团。



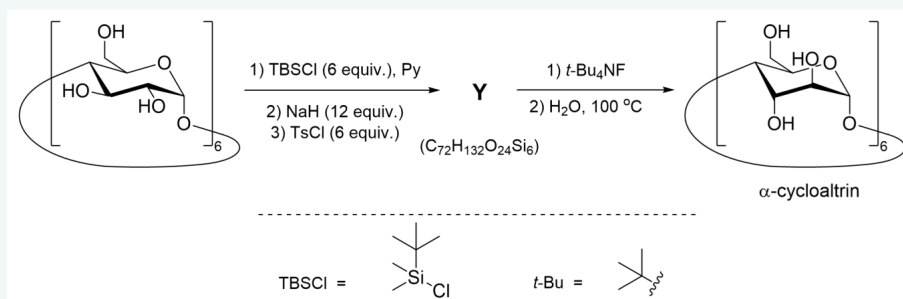
equiv.= 当量

9.2 勾选有利的椅式构象，并通过补全 CD 模板画出 **K** 的结构。明确表示其立体化学。6.0 分

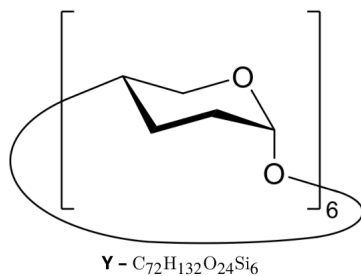


9.3 确定大环化合物 **X** 的环大小  $rs$ 。给出 **X** 中立体中心的数目  $sc$ 。8.0 分

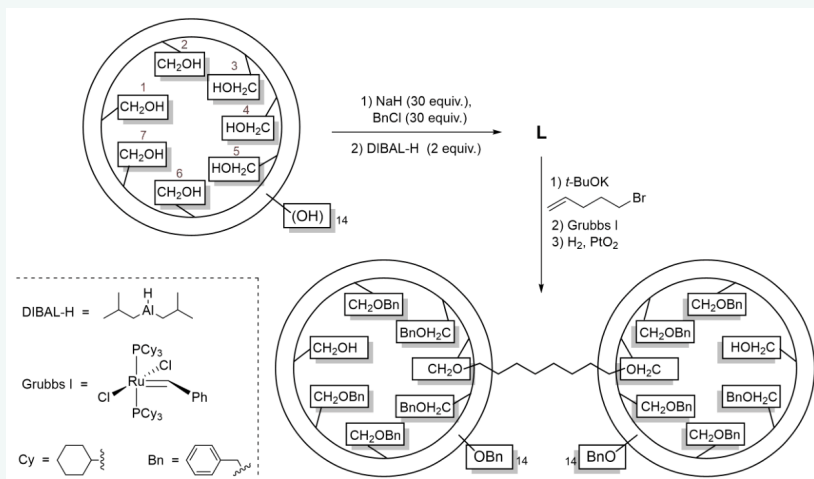
$\alpha$ -环阿卓糖是  $\alpha$ -CD 的合成类似物，其合成路线如下。



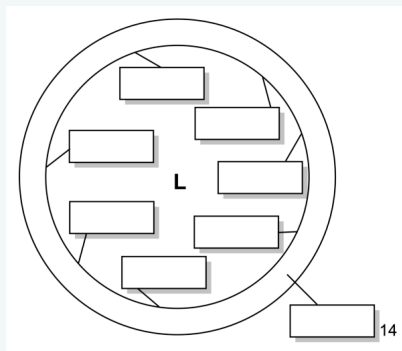
9.4 通过补全 CD 模板，画出 **Y** 的结构并表示其立体化学。3.0 分



2000 年, Sinay 等人证明, 单元 1 上的单个质子性基团 (NH 或 OH) 可将下一次伯羟基的还原脱苄基反应定向至大环中的单元 4 (若单元 4 的位置不可用, 则定向至单元 3)。借助这一性质, 他们合成了以下  $\beta$ -CD 二聚体, 产物为连接方式不同的构造异构体的混合物。

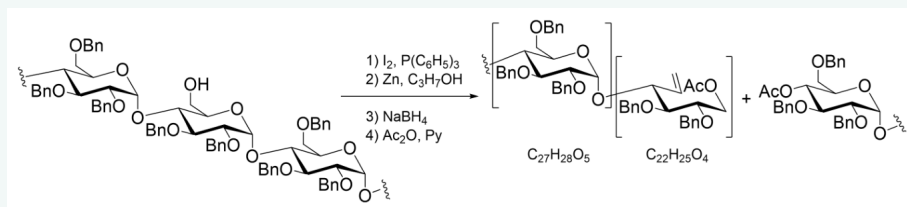


9.5 在  $\beta$ -CD 模板上画出 L 的结构。填写所有方框。2.0 分



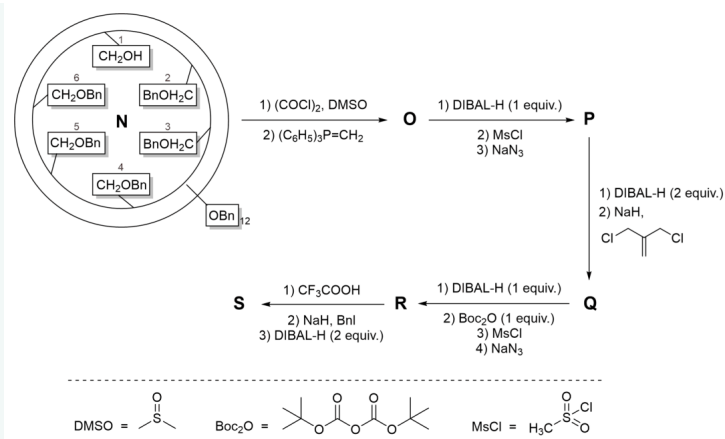
9.6 确定在 Sinay 等人的合成过程中可能形成的  $\beta$ -CD 二聚体异构体的数目。4.0 分

为确认脱苄基的位置, 对 L 进行了如下所示的“己-5-烯糖降解”反应。随后用质谱法分析产物。

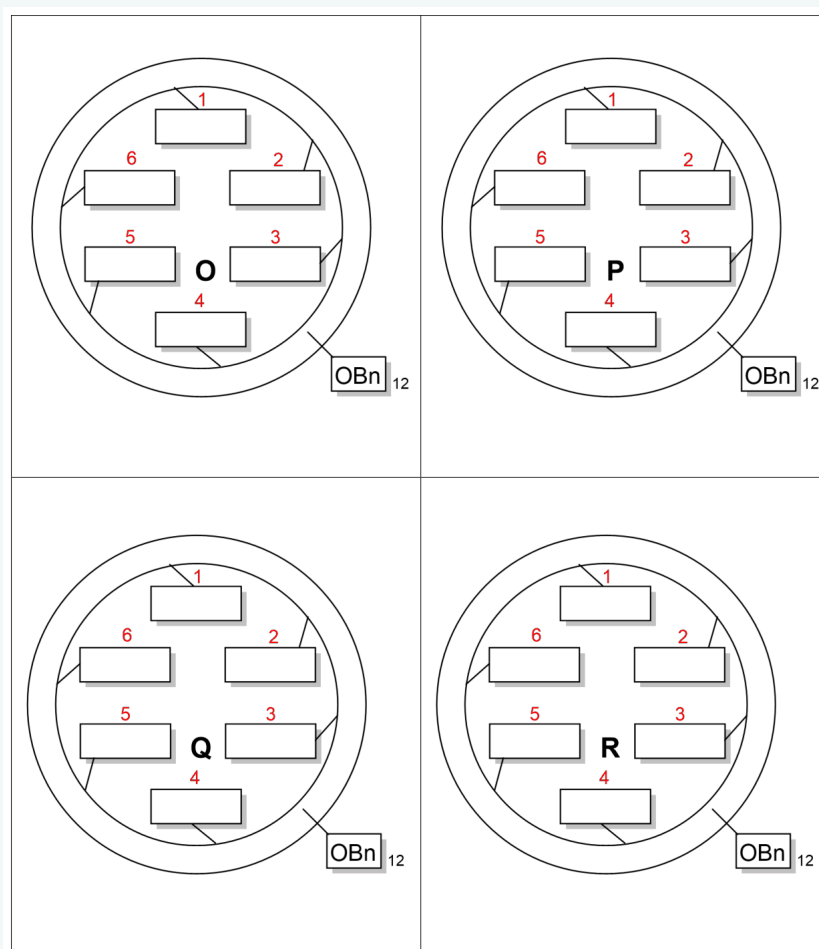


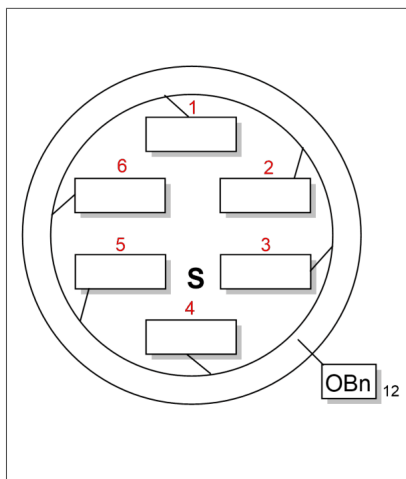
9.7 计算 L 的降解产物中观测到的两个  $[\text{M}^+\text{Na}]^+$  峰的  $m/z$  值。原子质量使用整数值。6.0 分

后来, Sollogoub 等人利用烯炔能将脱苄基反应定向至“邻位”吡喃葡萄糖单元的性质, 合成了六个单元分别具有不同修饰的  $\alpha$ -CD S:



9.8 在  $\alpha$ -CD 模板上画出 O-S 的结构。填写所有方框。必要时可将结构画在方框外。假设 1,2-单元修饰沿顺时针方向发生，而 1,3-单元修饰沿逆时针方向发生。质子性基团的定向效应强于烯烃。18.0 分





9.9 确定六个单元分别具有不同修饰的  $\alpha$ -CD 上官能团的所有可能排列的数目 (假设仅  $\text{CH}_2\text{OH}$  基团发生了修饰)。4.0 分

元素周期表

|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|-------------------|--|-------------------|--|-------------------|--|-------------------|--|-------------------|--|-------------------|--|-------------------|--|-------------------|--|-------------------|--|-------------------|--|-------------------|--|-------------------|--|-------------------|--|-------------------|--|-------------------|--|-------------------|--|-------------------|--|-------------------|--|--|--|
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  | 18                |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
| 1<br>H<br>1.008   |  | 2<br>He<br>4.003  |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
| 3<br>Li<br>6.94   |  | 4<br>Be<br>9.01   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  | 13<br>B<br>10.81  |  | 14<br>C<br>12.01  |  | 15<br>N<br>14.01  |  | 16<br>O<br>16.00  |  | 17<br>F<br>19.00  |  | 18<br>Ne<br>20.18 |  |                   |  |                   |  |                   |  |  |  |
| 11<br>Na<br>22.99 |  | 12<br>Mg<br>24.30 |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  | 13<br>Al<br>26.98 |  | 14<br>Si<br>28.09 |  | 15<br>P<br>30.97  |  | 16<br>S<br>32.06  |  | 17<br>Cl<br>35.45 |  | 18<br>Ar<br>39.95 |  |                   |  |                   |  |                   |  |  |  |
| 19<br>K<br>39.10  |  | 20<br>Ca<br>40.08 |  | 21<br>Sc<br>44.96 |  | 22<br>Ti<br>47.87 |  | 23<br>V<br>50.94  |  | 24<br>Cr<br>52.00 |  | 25<br>Mn<br>54.94 |  | 26<br>Fe<br>55.85 |  | 27<br>Co<br>58.93 |  | 28<br>Ni<br>58.69 |  | 29<br>Cu<br>63.55 |  | 30<br>Zn<br>65.38 |  | 31<br>Ga<br>69.72 |  | 32<br>Ge<br>72.63 |  | 33<br>As<br>74.92 |  | 34<br>Se<br>78.97 |  | 35<br>Br<br>79.90 |  | 36<br>Kr<br>83.80 |  |  |  |
| 37<br>Rb<br>85.47 |  | 38<br>Sr<br>87.62 |  | 39<br>Y<br>88.91  |  | 40<br>Zr<br>91.22 |  | 41<br>Nb<br>92.91 |  | 42<br>Mo<br>95.95 |  | 43<br>Tc<br>-     |  | 44<br>Ru<br>101.1 |  | 45<br>Rh<br>102.9 |  | 46<br>Pd<br>106.4 |  | 47<br>Ag<br>107.9 |  | 48<br>Cd<br>112.4 |  | 49<br>In<br>114.8 |  | 50<br>Sn<br>118.7 |  | 51<br>Sb<br>121.8 |  | 52<br>Te<br>127.6 |  | 53<br>I<br>126.9  |  | 54<br>Xe<br>131.3 |  |  |  |
| 55<br>Cs<br>132.9 |  | 56<br>Ba<br>137.3 |  | 57-71             |  | 72<br>Hf<br>178.5 |  | 73<br>Ta<br>180.9 |  | 74<br>W<br>183.8  |  | 75<br>Re<br>186.2 |  | 76<br>Os<br>190.2 |  | 77<br>Ir<br>192.2 |  | 78<br>Pt<br>195.1 |  | 79<br>Au<br>197.0 |  | 80<br>Hg<br>200.6 |  | 81<br>Tl<br>204.4 |  | 82<br>Pb<br>207.2 |  | 83<br>Bi<br>209.0 |  | 84<br>Po<br>-     |  | 85<br>At<br>-     |  | 86<br>Rn<br>-     |  |  |  |
| 87<br>Fr<br>-     |  | 88<br>Ra<br>-     |  | 89-103            |  | 104<br>Rf<br>-    |  | 105<br>Db<br>-    |  | 106<br>Sg<br>-    |  | 107<br>Bh<br>-    |  | 108<br>Hs<br>-    |  | 109<br>Mt<br>-    |  | 110<br>Ds<br>-    |  | 111<br>Rg<br>-    |  | 112<br>Cn<br>-    |  | 113<br>Nh<br>-    |  | 114<br>Fl<br>-    |  | 115<br>Mc<br>-    |  | 116<br>Lv<br>-    |  | 117<br>Ts<br>-    |  | 118<br>Og<br>-    |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
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|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
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|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
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|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
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|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
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|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
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|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
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|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
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|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
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|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |
|                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |                   |  |  |  |

题目译自官方英文原文。

## 答案

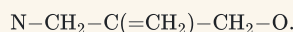
- 9.1:  $M(\beta\text{-CD}) = 1135.0 \text{ g mol}^{-1}$ 。
- 9.2: 勾选右侧的椅式构象,  $^1\text{C}_4$ 。K 为七(3,6-脱水)- $\beta$ -环糊精: 每个残基均具有一个  $\text{C3-O-C6}$  桥和一个游离的  $\text{C2-OH}$ 。
- 9.3:  $rs = 35$ ,  $sc = 21$ 。
- 9.4: Y 为  $\alpha$ -CD 的所有 6-O 位均受 TBS 保护、所有单元均为 2,3-脱水结构的甘露糖构型衍生物。每个环氧氧原子均与  $\text{C5-CH}_2\text{OTBS}$  取代基位于同一侧。
- 9.5: L: 伯位方框 1 和 4 填入  $\text{CH}_2\text{OH}$ ; 方框 2、3、5、6 和 7 填入  $\text{CH}_2\text{OBn}$ ; 外侧方框填入  $\text{OBn}$ , 重复 14 次。
- 9.6: 3 种连接方式不同的构造异构体。
- 9.7:  $m/z = 1299$  和  $1731$ 。
- 9.8: 完整的取代模式见下表。全部十二个仲位含氧取代基均保持为  $\text{OBn}$ 。
- 9.9: 120 种排列。

对于 9.8, 数字表示葡萄糖单元, 按答题纸上的顺时针方向编号。表中各项为连接在相应单元 C5 上的取代基。

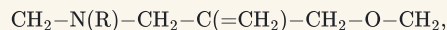
| 化合物 | 单元 1             | 单元 2                    | 单元 3                    | 单元 4                    | 单元 5                    | 单元 6                    |
|-----|------------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|
| O   | $\text{CH=CH}_2$ | $\text{CH}_2\text{OBn}$ | $\text{CH}_2\text{OBn}$ | $\text{CH}_2\text{OBn}$ | $\text{CH}_2\text{OBn}$ | $\text{CH}_2\text{OBn}$ |

| 化合物 | 单元 1               | 单元 2                           | 单元 3                | 单元 4                | 单元 5                    | 单元 6                            |
|-----|--------------------|--------------------------------|---------------------|---------------------|-------------------------|---------------------------------|
| P   | CH=CH <sub>2</sub> | CH <sub>2</sub> N <sub>3</sub> | CH <sub>2</sub> OBn | CH <sub>2</sub> OBn | CH <sub>2</sub> OBn     | CH <sub>2</sub> OBn             |
| Q   | CH=CH <sub>2</sub> | CH <sub>2</sub> NH, 桥的一端       | CH <sub>2</sub> OBn | CH <sub>2</sub> OBn | CH <sub>2</sub> O, 桥的一端 | CH <sub>2</sub> OBn             |
| R   | CH=CH <sub>2</sub> | CH <sub>2</sub> N(Boc), 桥的一端   | CH <sub>2</sub> OBn | CH <sub>2</sub> OBn | CH <sub>2</sub> O, 桥的一端 | CH <sub>2</sub> N <sub>3</sub>  |
| S   | CH=CH <sub>2</sub> | CH <sub>2</sub> N(Bn), 桥的一端    | CH <sub>2</sub> OH  | CH <sub>2</sub> OBn | CH <sub>2</sub> O, 桥的一端 | CH <sub>2</sub> NH <sub>2</sub> |

在 Q、R 和 S 中，将单元 2 上所标示的氮原子与单元 5 上的氧原子通过下列结构连接：



因此，从单元 2 到单元 5 的完整桥结构为



其中  $R = \text{H}$ 、Boc 和 Bn，分别对应 Q、R 和 S。

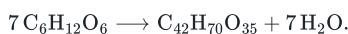
## 解答

下列 SMILES 指定了完整的分子连接关系和立体化学。椅式构象以及在印制模板上的位置另用文字说明。

取代基的缩写为：苄基，Bn, \*Cc1ccccc1；乙酰基，Ac, \*C(=O)C；叔丁基二甲基硅基，TBS, \*[Si](C)(C)C(C)(C)C；叔丁氧羰基，Boc, \*C(=O)OC(C)(C)C。这里的 \* 表示取代基的连接点。

### 9.1

七个葡萄糖分子构成的环状结构含有七个糖苷键。因此，形成  $\beta$ -CD 时脱去七个水分子：



使用所给的原子质量，

$$M(\text{H}_2\text{O}) = 2(1.008) + 16.00 = 18.016 \text{ g mol}^{-1},$$

因此

$$\begin{aligned} M(\beta\text{-CD}) &= 7(180.16) - 7(18.016) \\ &= 1135.008 \text{ g mol}^{-1} \\ &\approx \boxed{1135.0 \text{ g mol}^{-1}}. \end{aligned}$$

$\alpha$ -D-吡喃葡萄糖形式的葡萄糖的 SMILES 为 OC[C@H]1O[C@H](O)[C@H](O)[C@@H](O)[C@@H]1O；水的 SMILES 为 O。

$\beta$ -环糊精，C\_{42}H\_{70}O\_{35}，其 SMILES 为：

OC[C@H]1O[C@@H]2O[C@@H]3[C@H](O)[C@@H](O)[C@@H](O[C@@H]4[C@H](O)[C@@H](O)[C@@H](O[C@@H]5[C@H](O)[C@@H](O)[C@@H](O[C@@H]6[C@H](O)[C@@H](O)[C@@H](O[C@@H]7[C@H](O)[C@@H](O)[C@@H](O[C@@H]8[C@H](O)[C@@H](O)[C@@H](O[C@@H]1[C@H](O)[C@@H]2O)O[C@@H]8CO)O[C@@H]7CO)O[C@@H]6CO)O[C@@H]5CO)O[C@@H]4CO)O[C@@H]3CO

### 9.2

七当量的对甲苯磺酰氯优先活化七个 C6 伯羟基。在碱性条件下，每个葡萄糖残基的 C3 醇盐氧通过分子内  $S_N2$  取代反应进攻自身的 C6 碳原子，使对甲苯磺酸根离去。这一过程生成了 **3,6-脱水醚桥**。

C2 羟基保持游离状态。取代发生在不构成立体中心的 C6 碳原子上，因此葡萄糖各立体中心的原有构型保持不变。

3,6 桥要求采用翻转后的  $^1C_4$  椅式构象，即右侧模板。补全方法如下：

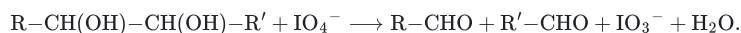
- 将 C5-C6 取代基置于环的上方。
- 将 C6 通过氧原子连接至 C3，同样位于环的上侧。
- 将剩余的 C2-OH 画成向下的直立键。
- 保留图中已给出的  $\alpha$ -糖苷键连接。

K, 七(3,6-脱水)- $\beta$ -环糊精，其分子式为 C\_{42}H\_{56}O\_{28}，SMILES 为：

O[C@H]1[C@H]2O[C@@H]3[C@@H]4OC[C@H]3O[C@H](O[C@@H]3[C@@H]5OC[C@H]3O[C@H](O[C@@H]3[C@@H]6OC[C@H]3O[C@H](O[C@@H]3[C@@H]7OC[C@H]3O[C@H](O[C@@H]3[C@@H]8OC[C@H]3O[C@H](O[C@@H]3[C@@H]9OC[C@H]3O[C@H](O[C@@H]3[C@@H]10C[C@H]3O2)[C@@H]9O)[C@@H]8O)[C@@H]7O)[C@@H]6O)[C@@H]5O)[C@@H]4O

### 9.3

由于 C2 和 C3 上的羟基构成邻二醇，高碘酸盐使每个葡萄糖残基的 C2-C3 键断裂。相应的一般原子衡算式为



硼氢化物将两个醛基均还原为伯醇。随后，乙酸酐使原 C2、C3 和 C6 位的羟基乙酰化。

C2-C3 键断裂后，穿过每个残基而仍然保留的大环路径为



沿此路径再连接至下一个残基的 C1。每个来源于葡萄糖的单元为大环贡献五个原子：

$$\boxed{rs = 7 \times 5 = 35}.$$

C2 和 C3 变为 CH\_2OAc 基团，失去其立体化学特征。C1、C4 和 C5 的构型保留：

$$\boxed{sc = 7 \times 3 = 21}.$$

X 是经高碘酸盐裂解、还原并全乙酰化的  $\beta$ -环糊精衍生物，其分子式为 C\_{84}H\_{126}O\_{56}，SMILES 为：



$$\left(\frac{m}{z}\right)_3 = 1276 + 23 = 1299, \quad \left(\frac{m}{z}\right)_4 = 1708 + 23 = 1731.$$

中性片段的分子式分别为  $C_{78}H_{84}O_{16}$  和  $C_{105}H_{112}O_{21}$ 。

**三单元降解片段的钠加合离子**， $[C_{78}H_{84}O_{16} + Na]^+$ ，其 SMILES 为：

C=C[C@H](O[C@H]1O[C@H](COCC2CCCCC2)[C@H](O[C@H]2O[C@H](COCC3CCCCC3)[C@H](OC(C)=O)[C@H](OCc3CCCCC3)[C@H]2OCc2CCCCC2)[C@H](OCc2CCCCC2)[C@H]1OCc1CCCCC1)[C@H](OCc1CCCCC1)[C@H](COC(C)=O)OCc1CCCCC1.[Na+]

**四单元降解片段的钠加合离子**， $[C_{105}H_{112}O_{21} + Na]^+$ ，其 SMILES 为：

C=C[C@H](O[C@H]1O[C@H](COCC2CCCCC2)[C@H](O[C@H]2O[C@H](COCC3CCCCC3)[C@H](O[C@H]3O[C@H](COCC4CCCCC4)[C@H](OC(C)=O)[C@H](OCc4CCCCC4)[C@H]3OCc3CCCCC3)[C@H](OCc3CCCCC3)[C@H]2OCc2CCCCC2)[C@H](OCc2CCCCC2)[C@H]1OCc1CCCCC1)[C@H](OCc1CCCCC1)[C@H](COC(C)=O)OCc1CCCCC1.[Na+]

这些 SMILES 中未与其他部分连接的钠组分子用于指定加合离子的组成；题目并未确定具体的钠配位几何构型。

## 9.8

在整个反应序列中，十二个仲位苄醚基团均保持完整。

**O 的形成**。Swern 氧化将单元 1 上的游离  $CH_2OH$  基团转化为醛基。随后，Wittig 亚甲基化将该侧链转化为  $CH=CH_2$ 。单元 2–6 保留  $CH_2OBn$ 。

**O** 是单元 1 带有乙烯基的  $\alpha$ -环糊精衍生物，其 SMILES 为：

C=C[C@H]1O[C@@H]2O[C@@H]3[C@H](OCc4CCCCC4)[C@@H](OCc4CCCCC4)[C@@H](O[C@@H]4[C@H](OCc5CCCCC5)[C@@H](OCc5CCCCC5)[C@@H](O[C@@H]5[C@H](OCc6CCCCC6)[C@@H](OCc6CCCCC6)[C@@H](O[C@@H]6[C@H](OCc7CCCCC7)[C@@H](OCc7CCCCC7)[C@@H](O[C@@H]7[C@H](OCc8CCCCC8)[C@@H](OCc8CCCCC8)[C@@H](O[C@@H]1[C@H](OCc1CCCCC1)[C@H]2OCc1CCCCC1)O[C@@H]7COCc1CCCCC1)O[C@@H]6COCc1CCCCC1)O[C@@H]5COCc1CCCCC1)O[C@@H]4COCc1CCCCC1)O[C@@H]3COCc1CCCCC1

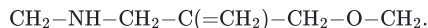
**P 的形成**。单元 1 上的烯烃将第一次脱苄基定向至其顺时针方向的相邻单元，即单元 2。先进行甲磺酰化，再由叠氮离子取代，使所生成的  $CH_2OH$  转化为  $CH_2N_3$ 。

**P** 是 **O** 的单元 2 叠氮甲基衍生物，其 SMILES 为：

C=C[C@H]1O[C@@H]2O[C@@H]3[C@H](OCc4CCCCC4)[C@@H](OCc4CCCCC4)[C@@H](O[C@@H]4[C@H](OCc5CCCCC5)[C@@H](OCc5CCCCC5)[C@@H](O[C@@H]5[C@H](OCc6CCCCC6)[C@@H](OCc6CCCCC6)[C@@H](O[C@@H]6[C@H](OCc7CCCCC7)[C@@H](OCc7CCCCC7)[C@@H](O[C@@H]7[C@H](OCc8CCCCC8)[C@@H](OCc8CCCCC8)[C@@H](O[C@@H]1[C@H](OCc1CCCCC1)[C@H]2OCc1CCCCC1)O[C@@H]7COCc1CCCCC1)O[C@@H]6COCc1CCCCC1)O[C@@H]5COCc1CCCCC1)O[C@@H]4COCc1CCCCC1)O[C@@H]3CN=[N+]=[N-]

**Q 的形成**。DIBAL-H 首先将单元 2 上的叠氮基还原为伯氨基。其质子性  $NH$  基团随后将脱苄基定向至相对的单元，即单元 5。

因此，两个可参与反应的基团分别为单元 2 上的  $CH_2NH_2$  和单元 5 上的  $CH_2OH$ 。它们与 1,3-二氯-2-亚甲基丙烷 ( $C=C(CC1)CC1$ ) 反应，通过  $N,O$  桥连接起来：



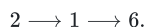
其中仍保留一个  $N-H$  键，因此氮原子可以对下一次脱苄基起定向作用。

**Q** 是单元 2 与单元 5 之间具有  $N,O$  桥的  $\alpha$ -环糊精衍生物，其 SMILES 为：

C=C[C@H]1O[C@@H]2O[C@@H]3[C@H](OCc4CCCCC4)[C@@H](OCc4CCCCC4)[C@H]4O[C@@H]5[C@H](OCc6CCCCC6)[C@@H](OCc6CCCCC6)[C@@H](O[C@@H]6[C@H](OCc7CCCCC7)[C@@H](OCc7CCCCC7)[C@@H](O[C@@H]7[C@H](OCc8CCCCC8)[C@@H](OCc8CCCCC8)[C@@H](O[C@@H]8[C@H](OCc9CCCCC9)[C@@H](OCc9CCCCC9)[C@@H](O[C@@H]1[C@H](OCc1CCCCC1)[C@H]2OCc1CCCCC1)O[C@@H]8COCc1CCCCC1)O[C@@H]7COC(=C)CNC[C@H]3O4)O[C@@H]6COCc1CCCCC1)O[C@@H]5COCc1CCCCC1

**R 的形成**。单元 2 上仲胺的  $NH$  是定向作用最强的基团。其通常的 1,4 位目标，即单元 5，已参与成桥，没有可脱除的苄醚基团。

因此，替代路径是从单元 2 沿逆时针方向进行 1,3 位修饰：



DIBAL-H 使单元 6 上的伯羟基脱保护而显露出来。Boc 保护使桥上的氮原子被封固，同时通过甲磺酰化和叠氮离子取代，将新显露的单元 6 侧链转化为  $CH_2N_3$ 。

**R** 是 **Q** 经  $N$ -Boc 保护、单元 6 带有叠氮甲基的衍生物，其 SMILES 为：

C=C[C@H]1O[C@@H]2O[C@@H]3[C@H](OCc4CCCCC4)[C@@H](OCc4CCCCC4)[C@H]4O[C@@H]5[C@H](OCc6CCCCC6)[C@@H](OCc6CCCCC6)[C@@H](O[C@@H]6[C@H](OCc7CCCCC7)[C@@H](OCc7CCCCC7)[C@@H](O[C@@H]7[C@H](OCc8CCCCC8)[C@@H](OCc8CCCCC8)[C@@H](O[C@@H]8[C@H](OCc9CCCCC9)[C@@H](OCc9CCCCC9)[C@@H](O[C@@H]1[C@H](OCc1CCCCC1)[C@H]2OCc1CCCCC1)O[C@@H]8CN=[N+]=[N-])O[C@@H]7COC(=C)CN(C(=O)OC(C)(C)C)[C@H]3O4)O[C@@H]6COCc1CCCCC1)O[C@@H]5COCc1CCCCC1

**S 的形成**。三氟乙酸脱去 Boc。随后进行苄基化，将桥上的氮转化为  $N$ -苄基叔胺，从而消除其  $N-H$  定向基团。

DIBAL-H 将单元 6 上的叠氮基还原为  $CH_2NH_2$ 。这一新生成的质子性基团将脱苄基定向至相对的单元，即单元 3，在该处生成  $CH_2OH$ 。单元 4 保留其伯位苄醚基团。

因此，最终的六条侧链各不相同，按顺时针顺序依次为：乙烯基、桥连的  $N$ -苄基氨基、羟甲基、苄氧甲基、桥连的氧甲基和氧甲基。

**S** 是六个单元分别具有不同修饰的  $\alpha$ -环糊精衍生物，其 SMILES 为：

C=C[C@H]1O[C@@H]2O[C@@H]3[C@H](OCc4CCCCC4)[C@@H](OCc4CCCCC4)[C@H]4O[C@@H]5[C@H](OCc6CCCCC6)[C@@H](OCc6CCCCC6)[C@@H](O[C@@H]6[C@H](OCc7CCCCC7)[C@@H](OCc7CCCCC7)[C@@H](O[C@@H]7[C@H](OCc8CCCCC8)[C@@H](OCc8CCCCC8)[C@@H](O[C@@H]8[C@H](OCc9CCCCC9)[C@@H](OCc9CCCCC9)[C@@H](O[C@@H]1[C@H](OCc1CCCCC1)[C@H]2OCc1CCCCC1)O[C@@H]8CN)O[C@@H]7COC(=C)CN(Cc1CCCCC1)[C@H]3O4)O[C@@H]6COCc1CCCCC1)O[C@@H]5CO

## 9.9

将六个不同的取代基分配到六个带标号的位点上，共有  $6!$  种方式。旋转整个  $\alpha$ -CD 环不会产生新的排列，因此每种排列都被计数了六次：

$$N = \frac{6!}{6} = 5! = \boxed{120}.$$

不需要再除以二。将环上的顺序反向，并不是具有方向性和手性的  $\alpha$ -D-吡喃葡萄糖苷骨架的对称操作。

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解答已与官方解答核对。