1. 单一選擇題 每題 4 分，共計 60 分

E (1) The following data were obtained for the reaction

\[ 2\text{ClO}_2(aq) + 2\text{OH}^-(aq) \rightarrow \text{ClO}_3^-(aq) + \text{ClO}_2^-(aq) + \text{H}_2\text{O}(l) \]

<table>
<thead>
<tr>
<th>[ClO_2] (M)</th>
<th>[OH^-] (M)</th>
<th>initial rate (M/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.060</td>
<td>0.030</td>
</tr>
<tr>
<td>2</td>
<td>0.020</td>
<td>0.030</td>
</tr>
<tr>
<td>3</td>
<td>0.020</td>
<td>0.090</td>
</tr>
</tbody>
</table>

What is the overall order of the reaction?

(A) 4  (B) 0  (C) 1  (D) 2  (E) 3

A (2) A first-order reaction has a rate constant of 0.33 min\(^{-1}\). It takes _____ min for the reactant concentration to decrease from 0.13 M to 0.088 M.

(A) 1.2  (B) 1.4  (C) 0.51  (D) 0.13  (E) 0.85

C (3) A possible mechanism for the overall reaction \( \text{Br}_2(g) + 2\text{NO}(g) \rightarrow 2\text{NOBr}(g) \) is

\[
\begin{align*}
\text{Br}_2(g) + \text{NO}(g) & \rightarrow 2\text{NOBr}(g) & \text{(fast)} \\
\text{NOBr}_2(g) + \text{NO}(g) & \rightarrow 2\text{NOBr}(g) & \text{(slow)} \\
\end{align*}
\]

The rate law for formation of NOBr based on this mechanism is rate = \( \ldots \).

(A) \( k_1[\text{NO}]^{1/2} \)  (B) \( k_1[\text{Br}_2]^{1/2} \)  (C) \( (k_2/k_1)[\text{NO}]^2[\text{Br}_2] \)
(D) \( (k_1/k_2)^2[\text{NO}]^2 \)  (E) \( (k_2/k_1)[\text{NO}][\text{Br}_2]^2 \)

E (4) Consider the following reaction: \( \text{H}_2(g) + \text{I}_2(g) \rightarrow 2\text{HI}(g) \)
At equilibrium in a particular experiment, the concentrations of \( \text{H}_2, \text{I}_2, \) and \( \text{HI} \) were 0.15 M, 0.033 M, and 0.55 M, respectively. The value of \( K_{eq} \) for this reaction is

(A) 23  (B) 111  (C) 9.0 \times 10^{-3}  (D) 6.1  (E) 61

B (5) Consider the following reaction at equilibrium: \( 2\text{NH}_3(g) \rightarrow 3\text{H}_2(g) + \text{N}_2(g) \)
Le Châlterlier’s principle predicts that the moles of \( \text{H}_2 \) in the reaction container will increase with _____

(A) removal of \( \text{NH}_3 \) from the reaction vessel (V and T constant).
(B) a decrease in the total pressure (T constant).
(C) addition of some \( \text{N}_2 \) to the reaction vessel (V and T constant).
(D) a decrease in the total volume of the reaction vessel (T constant).
(E) an increase in total pressure by the addition of He gas (V and T constant).

D (6) The effect of a catalyst on an equilibrium is to _____

(A) increase the rate of the forward reaction only.
(B) increase the equilibrium constant so that products are favored.
(C) slow the reverse reaction only.
(D) increase the rate at which equilibrium is achieved without changing the composition of the equilibrium mixture.
(E) shift the equilibrium to the right.
(7) The $K_a$ for hypochlorous acid (HClO) is $3.0 \times 10^{-8}$. What is the pH at 25°C of an aqueous solution that is 0.020 M in HClO?

(A) +2.45  (B) -2.45  (C) -9.22  (D) +9.22  (E) +4.61

(8) In the reaction BF$_3$ + F$^-$ → BF$_4^-$, BF$_3$ acts as a(n) _______.

(A) Arrhenius acid  (B) Arrhenius base  (C) Brønsted acid  (D) Lewis acid  (E) Lewis base

(9) Of the following substances, an aqueous solution of _______ will form basic Solution.

(i) NH$_4$Cl,  (ii) Ca(NO$_3$)$_2$,  (iii) K$_2$CO$_3$,  (iv) NaF

(A) i and ii  (B) i and iii  (C) iv only  (D) iii and iv  (E) i only

(10) The pH of a solution prepared by mixing 45 mL of 0.183 M KOH and 65 mL of 0.145 M HCl is ________.

(A) 1.31  (B) 2.92  (C) 0.74  (D) 1.97  (E) 4.15

(11) Which compound listed below has the greatest molar solubility in water?

(A) ZnCO$_3$ ($K_{sp} = 1.4 \times 10^{-11}$)  (B) Cd(OH)$_2$ ($K_{sp} = 2.5 \times 10^{-14}$)

(C) Cd CO$_3$ ($K_{sp} = 5.2 \times 10^{-12}$)  (D) AgI ($K_{sp} = 8.3 \times 10^{-17}$)

(E) CaF$_2$ ($K_{sp} = 3.9 \times 10^{-11}$)

(12) For which salt should the aqueous solubility be most sensitive to pH?

(A) Ca(NO$_3$)$_2$  (B) CaF$_2$  (C) CaCl$_2$  (D) CaBr$_2$  (E) CaI$_2$

(13) Why is carbon monoxide toxic?

(A) It causes renal failure  
(B) It binds to hemoglobin, thus blocking the transport of oxygen  
(C) It blocks acetylcholine receptor sites causing paralysis and rapid death  
(D) It induces leukemia  
(E) It binds to oxygen and cause suffocation

(14) Select the substance that is thought to be partially responsible for depleting the concentration of ozone in the stratosphere?

(A) CFCl$_3$  (B) CO$_2$  (C) CO  (D) N$_2$  (E) He

(15) $\Delta S$ is positive for the reaction __________

(A) CaO(s) + CO$_2$(g) → CaCO$_3$(s)  (B) N$_2$(g) + 3H$_2$(g) → 2NH$_3$(g)

(C) 2SO$_3$(g) → 2SO$_2$(g) + O$_2$(g)  (D) Ag$^+$(aq) + Cl$^-$ (aq) → AgCl(s)

(E) H$_2$O(l) → H$_2$O(s)
2. The gas-phase decomposition of NO₂, NO₂(g) → NO(g) + O₂(g), is studied at 383°C, giving the following data:

<table>
<thead>
<tr>
<th>time (s)</th>
<th>[NO₂] (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0.100</td>
</tr>
<tr>
<td>5.0</td>
<td>0.017</td>
</tr>
<tr>
<td>10.0</td>
<td>0.0090</td>
</tr>
<tr>
<td>15.0</td>
<td>0.0062</td>
</tr>
<tr>
<td>20.0</td>
<td>0.0047</td>
</tr>
</tbody>
</table>

(a) Is the reaction first order or second order with respect to the concentration of NO₂?
(b) What is the value of the rate constant? (6 分)

3. The first–order rate constant for reaction of a particular organic compound with water varies with temperature as follows:

<table>
<thead>
<tr>
<th>temperature (K)</th>
<th>rate constant (s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>3.2 × 10⁻¹¹</td>
</tr>
<tr>
<td>320</td>
<td>1.0 × 10⁻⁹</td>
</tr>
<tr>
<td>340</td>
<td>3.0 × 10⁻⁸</td>
</tr>
<tr>
<td>355</td>
<td>2.4 × 10⁻⁷</td>
</tr>
</tbody>
</table>

From these data calculate the activation energy in units of kJ/mol. (6 分)
4. For the reaction \( \text{I}_2(\text{g}) + \text{Br}_2(\text{g}) \rightleftharpoons 2\text{IBr}(\text{g}) \), \( K_{\text{eq}} = 280 \) at 150°C. Suppose that 0.500 mol IBr in a 1.00-L flask is allowed to reach equilibrium at 150°C. What are the equilibrium partial pressures of IBr, I\(_2\) and Br\(_2\)?

\[
K_{\text{eq}} = \frac{P^2_{\text{IBr}}}{P_{\text{I}_2} \times P_{\text{Br}_2}} = 280
\]

\[
P_{\text{IBr}} = \frac{nRT}{V} = \frac{0.500 \text{ mol}}{1.000 \text{ L}} \times 423 \text{ K} \times 0.08206 \frac{\text{L atm}}{\text{K mol}} = 17.4 \text{ atm}
\]

Since no I\(_2\) or Br\(_2\) were present initially, the amounts present at equilibrium are produced by the reverse reaction and stoichiometrically equal. Let these amounts equal \( x \). The amount of HBr that reacts is then 2\( x \). Substitute the equilibrium pressures (in terms of \( x \)) into the equilibrium expression and solve for \( x \).

\[
\begin{align*}
\text{initial} & : 0 \text{ atm} \quad 0 \text{ atm} \quad 17.356 \\
\text{change} & : +x \text{ atm} \quad +x \text{ atm} \quad -2x \\
\text{equil} & : x \text{ atm} \quad x \text{ atm} \quad (17.356 - 2x) \text{ atm}
\end{align*}
\]

\[
K_{\text{eq}} = 280 = \frac{(17.356 - 2x)^2}{x^2} \quad \text{taking the square root of both sides}
\]

\[
16.733 = \frac{17.356 - 2x}{x} \quad 16.733x + 2x = 17.356; \quad 18.733x = 17.356
\]

\[
x = 0.926 \text{ atm}; \quad P_{\text{I}_2} = 0.926 \text{ atm}; \quad P_{\text{Br}_2} = 0.926 \text{ atm}
\]

\[
P_{\text{IBr}} = 17.356 - 2x = 17.356 - 1.853 = 15.503 = 15.5 \text{ atm}
\]

\[
\text{Check: } \frac{(15.5)^2}{(0.926)^2} = 280. \text{ Our values are self-consistent.}
\]

5. Ephedrine, a central nervous system stimulant, is used in nasal sprays as a decongestant. This compound is a weak organic base:

\[
\text{C}_{10}\text{H}_{15}\text{ON}^{\text{(aq)}} + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{C}_{10}\text{H}_{15}\text{ONH}^{+}(\text{aq}) + \text{OH}^{-}(\text{aq})
\]

A 0.035 M solution of ephedrine has a pH of 11.33. (a) What are the equilibrium concentrations of \( \text{C}_{10}\text{H}_{15}\text{ON} \), \( \text{C}_{10}\text{H}_{15}\text{ONH}^{+} \), and \( \text{OH}^{-} \)? (b) Calculate \( K_b \) for ephedrine.

(a) \[
[\text{OH}^{-}] = 10^{-pOH} = 10^{-4.00} = 14.00 - 11.33 = 2.67
\]

\[
[\text{OH}^{-}] = 10^{-2.67} = 2.138 \times 10^{-3} = 2.1 \times 10^{-3} \text{ M}
\]

\[
\text{C}_{10}\text{H}_{15}\text{ON(aq)} + \text{H}_2\text{O(l)} \rightleftharpoons \text{C}_{10}\text{H}_{15}\text{ONH}^{+}(\text{aq}) + \text{OH}^{-}(\text{aq})
\]

\[
\begin{array}{c|c|c|c}
\text{initial} & 0.035 \text{ M} & 0 & 0 \\
\hline
\text{equil.} & 0.033 \text{ M} & 2.1 \times 10^{-3} \text{ M} & 2.1 \times 10^{-3} \text{ M}
\end{array}
\]

(b) \[
K_b = \frac{[\text{C}_{10}\text{H}_{15}\text{ONH}^{+}] \times [\text{OH}^{-}]}{[\text{C}_{10}\text{H}_{15}\text{ON}]} = \frac{(2.138 \times 10^{-3})^2}{0.033286} = 1.4 \times 10^{-4}
\]
6. A buffer solution contains 0.10 mol of acetic acid and 0.13 mol of sodium acetate in 1.00 L of water. (a) What is the pH of this buffer? (b) What is the pH of the buffer after the addition of 0.02 mol of KOH? \( K_a = 1.8 \times 10^{-5} \) for acetic acid

(a) \( K_a = \frac{[H^+][C_2H_3O_2^-]}{[HC_2H_3O_2]} \); \( [H^+] = \frac{K_a[H_2C_2O_2]}{[C_2H_3O_2^-]} \)

\[ [H^+] = \frac{1.8 \times 10^{-5} \times 0.10}{0.13} = 1.385 \times 10^{-5} = 1.4 \times 10^{-5} \text{ M}; \text{ pH} = 4.86 \]

(b) \[ \text{HC}_2\text{H}_3\text{O}_2\text{(aq)} + \text{KOH(aq)} \rightarrow \text{C}_2\text{H}_3\text{O}_2^-\text{(aq)} + \text{H}_2\text{O(l)} + \text{K}^\text{+}(\text{aq}) \]

\begin{align*}
0.10 \text{ mol} & \quad 0.02 \text{ mol} & \quad 0.13 \text{ mol} \\
-0.02 \text{ mol} & \quad -0.02 \text{ mol} & \quad +0.02 \text{ mol} \\
0.08 \text{ mol} & \quad 0 \text{ mol} & \quad 0.15 \text{ mol}
\end{align*}

\[ [H^+] = \frac{1.8 \times 10^{-5} \times 0.08 \text{ mol}}{0.15 \text{ mol}} = 9.60 \times 10^{-6} = 1 \times 10^{-5} \text{ M}; \text{ pH} = 5.02 \]

7. Use the following data to estimate the boiling point of benzene \((\text{C}_6\text{H}_6)\).

<table>
<thead>
<tr>
<th>Substance</th>
<th>( \Delta H^\circ ) (kJ/mol)</th>
<th>( \Delta G^\circ ) (kJ/mol)</th>
<th>( S^\circ ) (J/mol-K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{C}_6\text{H}_6(g) )</td>
<td>82.9</td>
<td>129.7</td>
<td>269.2</td>
</tr>
<tr>
<td>( \text{C}_6\text{H}_6(l) )</td>
<td>49.0</td>
<td>124.5</td>
<td>172.8</td>
</tr>
</tbody>
</table>

\[ \Delta S^\circ_{\text{vap}} = \frac{\Delta H^\circ_{\text{vap}}}{T_b}; \quad T_b = \frac{\Delta H^\circ_{\text{vap}}}{\Delta S^\circ_{\text{vap}}} \]

\[ \Delta H^\circ_{\text{vap}} = \Delta H^\circ_{\text{C}_6\text{H}_6(g)} - \Delta H^\circ_{\text{C}_6\text{H}_6(l)} = 82.9 - 49.0 = 33.9 \text{ kJ} \]

\[ \Delta S^\circ_{\text{vap}} = S^\circ_{\text{C}_6\text{H}_6(g)} - S^\circ_{\text{C}_6\text{H}_6(l)} = 269.2 - 172.8 = 96.4 \text{ J/K} \]

\[ T_b = 33.9 \times 10^3 \text{ J/96.4 K} = 351.66 = 352 \text{ K} = 79^\circ \text{C} \]

8. Consider the decomposition of barium carbonate: \( \text{BaCO}_3(s) \rightleftharpoons \text{BaO} + \text{CO}_2(g) \)

Using the following data, calculate the equilibrium pressure of \( \text{CO}_2 \) at (a) 25°C and (b) 737°C.

<table>
<thead>
<tr>
<th>Substance</th>
<th>( \Delta H^\circ ) (kJ/mol)</th>
<th>( \Delta G^\circ ) (kJ/mol)</th>
<th>( S^\circ ) (J/mol-K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{BaCO}_3(s) )</td>
<td>-1216.3</td>
<td>-1137.6</td>
<td>112.1</td>
</tr>
<tr>
<td>( \text{BaO} )</td>
<td>-553.5</td>
<td>-525.1</td>
<td>70.42</td>
</tr>
<tr>
<td>( \text{CO}_2 )</td>
<td>-393.5</td>
<td>-394.4</td>
<td>213.6</td>
</tr>
</tbody>
</table>

\[ \Delta H^\circ = \Delta H^\circ_{\text{BaO}} + \Delta H^\circ_{\text{CO}_2} - \Delta H^\circ_{\text{BaCO}_3} \]

\[ = -553.5 - 393.5 - (-1216.3) = 269.3 \text{ kJ} \]

\[ \Delta S^\circ = S^\circ_{\text{BaO}} + S^\circ_{\text{CO}_2} - S^\circ_{\text{BaCO}_3} \]

\[ = 70.42 + 213.6 - 112.1 = 171.82 \text{ J/K} = 0.1719 \text{ kJ/K} \]

(a) \[ \Delta G \text{ at } 298 \text{ K} = 269.3 \text{ kJ} - 298 \text{ K} (0.17192 \text{ kJ/K}) = 218.07 = 218.1 \text{ kJ} \]

\[ \ln K_w = \frac{-\Delta G^\circ}{RT} = \frac{-218.07 \times 10^3 \text{ J}}{8.314 \text{ J/K} \times 298 \text{ K}} = -88.017 = -88.02 \]

\[ K_w = 6.0 \times 10^{38}; \quad \text{P}_{\text{CO}_2} = 6.0 \times 10^{38} \text{ atm} \]

(b) \[ \Delta G \text{ at } 1100 \text{ K} = 269.3 \text{ kJ} - 1100 \text{ K} (0.17192 \text{ kJ/K}) = 680.2 \text{ kJ} \]

\[ \ln K_w = \frac{-\Delta G^\circ}{RT} = \frac{-680.19 \times 10^3 \text{ J}}{8.314 \text{ J/K} \times 1100 \text{ K}} = -8.768 = -8.77 \]

\[ K_w = 1.6 \times 10^{4}; \quad \text{P}_{\text{CO}_2} = 1.6 \times 10^{4} \text{ atm} \]