注意：考試開始鈴響前，不得翻閱試題，並不得書寫、畫記、作答。

國立清華大學 110 學年度碩士班考試入學試題

系所班組別：分析與環境科學研究所

科目代碼：2903
考試科目：物理化學

─作答注意事項─

1. 請核對答案卷（卡）上之准考證號、科目名稱是否正確。

2. 考試開始後，請於作答前先翻閱整份試題，是否有污損或試題印刷不清，得舉手請監試人員處理，但不得要求解釋題意。

3. 考生限在答案卷上標記「┏ 由此開始作答」區內作答，且不可書寫姓名、准考證號或與作答無關之其他文字或符號。

4. 答案卷用盡不得要求加頁。

5. 答案卷可用任何書寫工具作答，惟為方便閱卷辨識，請儘量使用藍色或黑色書寫；答案卡限用 2B 鉛筆畫記；如畫記不清（含未依範例畫記）致光學閱讀機無法辨識答案者，其後果一律由考生自行負責。

6. 其他應考規則、違規處理及扣分方式，請自行詳閱准考證明上「國立清華大學試場規則及違規處理辦法」，無法因本試題封面作答注意事項中未列明而稱未知悉。

1. Below is a list of five of the most important scientists in the field of physical chemistry. Describe the significance of their contributions and please mention it if he won a Nobel Prize. (20%)

   (1) James Prescott Joule (December 24, 1818 – October 11, 1889)

   (2) William Thomson 1st Baron Kelvin (June 26, 1824 – December 17, 1907)

   (3) Jacobus Henricus van't Hoff (August 30, 1852 – March 1, 1911)

   (4) Gilbert Newton Lewis (October 23, 1875 – March 23, 1946)

   (5) Henry Eyring (February 20, 1901 – December 26, 1981)

2. A sample of 1.0 mol $CH_3OH_{(g)}$ is condensed isothermally and reversibly to liquid at 64°C. The standard enthalpy of vaporization of methanol at 64°C is 35.3 kJ/mol. Find q, w, ΔU, ΔS, and ΔG for this process. (20%)

3. You have collected a tissue specimen that you would like to preserve by freeze drying. To ensure the integrity of the specimen, the temperature should not exceed -5.0 °C. The vapor pressure of ice at 273.16 K is 624 Pa. What is the maximum pressure at which the freeze drying can be carried out? The molar enthalpy changes of fusion of ice and vaporization of water are 6.01 and 40.66 kJ/mol, respectively. (20%)

4. The organic molecule benzene, C_6H_6, has a cyclic structure where the carbon atoms make a hexagon. The π electrons in the cyclic molecule can be approximated as having two-dimensional rotational motion. Calculate the diameter of this electron ring if it is assumed that a transition occurring at 260.0 nm corresponds to an electron going from $m = 3$ to $m = 4$. X-ray diffraction studies show that benzene is a completely flat and symmetrical molecule with all carbon-carbon and carbon-hydrogen bonds in benzene have lengths of 0.139 nm and 0.110 nm, respectively. Compare your result with the experimental data by X-ray and electron diffraction. (20%)
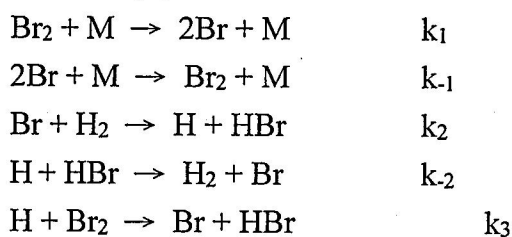
5. The $H_2 + Br_2$ reaction mechanism involves free radical carriers, molecules, or atoms with one or more unpaired electrons. Given the following possible elementary processes:

$$Br_2 + M \rightarrow 2Br + M \qquad k_1$$
$$2Br + M \rightarrow Br_2 + M \qquad k_{-1}$$
$$Br + H_2 \rightarrow H + HBr \qquad k_2$$
$$H + HBr \rightarrow H_2 + Br \qquad k_{-2}$$
$$H + Br_2 \rightarrow Br + HBr \qquad k_3$$

Show that the overall reaction rate is

$$\frac{d[HBr]}{dt} = \frac{A[H_2][Br_2]^{1/2}}{1 + B\dfrac{[HBr]}{[Br_2]}}$$

and in the process evaluate A and B in terms of $k_1, k_{-1}, k_2,.....$ (20%)