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 115 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：3003

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. 提早交卷者不可攜出試題，請將試題連同答案卷(卡)交予監考人員，攜出將以違規論處。當節考試結束後試題將置於講台，可自行取回，本試場不負保管責任。
7. 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。

國立清華大學 115 學年度碩士班考試入學試題

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考試科目（代碼）：物理化學（3003）

1. The high-temperature reservoir supplies the energy to run the engine, which produces some work and emits the remainder of the energy into a low-temperature reservoir. Draw a diagram of the type of engine and express its efficiency as a heat engine. Show that all reversible engines have the same efficiency regardless of their construction. (20%)

2. The discovery of the element argon by Lord Rayleigh and Sir William Ramsay had its origins in Rayleigh's measurements of the density of nitrogen with an eye toward accurate determination of its molar mass. Rayleigh prepared some samples of nitrogen by chemical reaction of nitrogen-containing compounds; under his standard conditions, a glass globe filled with this 'chemical nitrogen' had a mass of 2.2990 g. He prepared other samples by removing oxygen, carbon dioxide, and water vapor from atmospheric air; under the same conditions, this 'atmospheric nitrogen' had a mass of 2.3102 g. With the hindsight of knowing accurate values for the molar masses of nitrogen and argon, compute the mole fraction of argon in the atmospheric air on the assumption that the former was pure nitrogen, the latter a mixture of nitrogen and argon, and the partial pressure ratio of nitrogen to oxygen in the atmospheric air is approximately 3.71. (N: 14.01 g/mol, O: 16.00 g/mol, Ar: 39.95 g/mol) (20%)

3. Deduce the relation between the pressure (p) and mass density (ρ) of a perfect gas of molar mass M. Confirm graphically, using the following data on an ether at 298 K, that perfect behavior is reached at low pressures, and find the molar mass of the gas? Suggest a molecular formula of the ether. (20%)

p/(kPa)	12.223	25.20	36.97	60.37	85.23	101.3
ρ/(kg m^{-3})	0.225	0.456	0.664	1.062	1.468	1.734

4. NO, NO_2, CO, and ozone are major pollutants in a crowded city. When NO and NO_2 are present in sunlight, ozone formation occurs as a result of the photolysis of NO_2:

$$NO_2 + h\nu \xrightarrow{J_1} NO + O \quad \text{---------(1)}$$

$$O + O_2 + M \xrightarrow{k_2} O_3 + M \quad \text{---------(2)}$$

$$O_3 + NO \xrightarrow{k_3} NO_2 + O_2 \quad \text{---------(3)}$$

where j_1, k_2, and k_3 are the rate constants of equations 1, 2, and 3, respectively. Consider the dynamics of a system in which only these three reactions are taking place. Find a steady-state expression for the ozone concentration. If VOCs (volatile organic compounds) exist in the system, could you explain the role of volatile organic compounds in varying the ozone concentration? (20%)

5. Compute the freezing point temperature versus composition curve based on mole fraction for an ortho-chloronitrobenzene-para-chloronitrobenzene mixture. The physical properties for this system are given in Table 1. Calculate and mark the eutectic point. Sketch the liquid-solid phase diagram for this system and state what substances exist in each region. Assume negligible solid-solid solubility. (20%)

Table 1. Thermodynamic data

	ortho-chloronitrobenzene	para-chloronitrobenzene
Molecular weight (g/mol)	157.55	157.55
Density (g/mL)	1.368	1.52
Heat of fusion (kJ/mol)	19	20.8
Normal melting point (°C)	32.5	83.5