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 114 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. 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 114 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

考試科目（3003）：物理化學

1. The internal energy of a perfect monatomic gas relative to its value at T = 0 K is (3/2)nRT. Calculate (a) $(\partial P/\partial V)_T$ (b) $(\partial U/\partial P)_T$ (c) $(\partial H/\partial V)_T$ (d) $(\partial U/\partial T)_P$ (e) C_P-C_V (20%)

2. The following molar heat capacity data have been reported for L-alanine:

T/K	10	20	40	60	100	140	180	220	260	300
$C_{p,m}/(JK^{-1}mol^{-1})$	0.5	3.9	18	31	53	69	83	96	110	123

By a graphical treatment, obtain (a) the molar enthalpy of L-alanine at 300 K relative to its value at T = 0 and (b) the molar entropy of L-alanine at 300 K. (20%)

3. The expressions that apply to the treatment of refrigerators also describe the behaviour of heat pumps, where warmth is obtained from the back of a refrigerator while its front is being used to cool the outside world. Heat pumps are popular home heating devices because they are very efficient. Compare heating of a room at 295 K by each of two methods: (a) direct conversion of 1.00 kJ of electrical energy in an electrical heater, and (b) use of 1.00 kJ of electrical energy to run a reversible heat pump with the outside at 260 K. Discuss the origin of the difference in the energy delivered to the interior of the house by the two methods. (20%)

4. Cyclobutadiene, C_4H_4, is a four-carbon atom ring. Write the secular determinantal equation for the π molecular orbitals of this planar molecule. Find the Hückel molecular orbital energies and show the HOMO and LUMO. Predict the total π electronic energy of this compound. Is there extra π electron stabilization (as in butadiene or benzene) in this molecule? (20%)

5. Suppose that the enzyme E and substrate S combine to form a complex ES, which then dissociates into product P and free enzyme E. The product rate follows Michaelis-Menten form:

$$v = \frac{dp}{dt} = \frac{V_{max}[S]}{K_m + [S]}$$

In noncompetitive inhibition, the inhibitor I binds to a site other than the active site of the enzyme, so inhibitor I and substrate S can simultaneously bind to the enzyme, forming the ternary complex designated EIS. Binding of either inhibitor or substrate does not influence the affinity of either species to complex with the enzyme.

(a) Give a schematic representation of the model for the noncompetitive inhibition.

(b) If the dissociation constant of EI is K_I, please derive a rate expression for P formation with V_{max}, [S], K_m, [I], and K_I, by assuming quasi-steady state for [ES] and for [EI]. Draw a plot with 1/v against 1/[S] by varying [I]. (20%)