


**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 108 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(代碼)：物理化學(2903)

— 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. 作答中如有發現試題印刷不清，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。

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*請在【答案卷】作答

Fundamental constants

$c = 3.0 \times 10^8$ m/s, $e = 1.6 \times 10^{-19}$ C, $N_A = 6.02 \times 10^{23}$ mol⁻¹, $R = 0.082$ atm L/(K mol) = 8.314 J/(K mol), $k = 1.38 \times 10^{-23}$ J/K, $h = 6.626 \times 10^{-34}$ Js, $m_e = 9.11 \times 10^{-31}$ kg

- Each of the first three laws of thermodynamics (zeroth, first, and second) leads to the existence of a state function.
 - List the state function from each law.
 - It is nice to have a molecular picture of the macroscopic thermodynamic state functions. Interpret the microscopic nature of these state functions. (20%)
- Deduce the relation between the pressure 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
$\rho/\text{kg m}^{-3}$	0.225	0.456	0.664	1.062	1.468	1.734

- The molar heat capacity of anhydrous potassium hexacyanoferrate(II) varies with temperature as follows:

T/K	10	20	30	40	50	60	70	80	90	100
$C_{p,m}/\text{JK}^{-1}\text{mol}^{-1}$	2.1	14.4	36.4	62.6	87.0	111	131	149	165	180

Calculate the molar enthalpy at 100K relative to its value at $T = 0$ and the Third-Law entropy at 100K. (20%)

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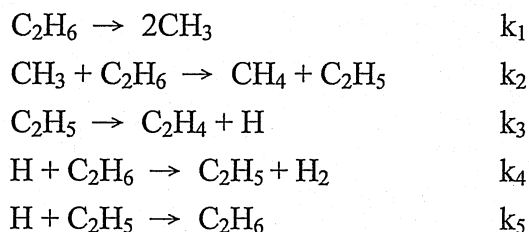
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*請在【答案卷】作答

4. Considering the dissociation reaction of dinitrogen tetroxide: $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$, the Gibbs energy changes of formation N_2O_4 and NO_2 (ΔG_f°) at 298 K are 97.89 kJ/mol and 51.31 kJ/mol, respectively. The reaction container maintains a constant pressure of 1 atm and a temperature of 298 K. The reaction is started with 1 mol of dinitrogen tetroxide only, so the amounts of N_2O_4 and NO_2 at a later time are given in terms of extent of reaction ξ by $n_{\text{N}_2\text{O}_4} = 1 - \xi$, and $n_{\text{NO}_2} = 2\xi$, respectively.
- (a) Derive the function of Gibbs energy of the reaction at 298K.
(b) Plot G versus ξ .
(c) Plot $dG/d\xi$ versus ξ .
(d) Plot $d^2G/d\xi^2$ versus ξ . (20%)
5. The Rice-Herzfeld mechanism for the dehydrogenation of ethane to ethylene and hydrogen showed that it led to first-order kinetics:

$$-\frac{d[\text{C}_2\text{H}_6]}{dt} = k_{app}[\text{C}_2\text{H}_6]$$

Given the following possible elementary processes:



Confirm this remark, find the approximations that lead to the rate law quoted there, and express k_{app} in terms of k_1, k_2, k_3, \dots . (20%)