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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Fundamental constants

$c = 3.0\times10^{8}$ m/s, $e = 1.6\times10^{-19}$ C, $N_A = 6.02\times10^{23}$ mol^{-1}, $R = 0.082$ atm L/(K mol) = 8.314 J/(K mol), $k = 1.38\times10^{-23}$ J/K, $h = 6.626\times10^{-34}$ Js, $m_e = 9.11\times10^{-31}$ kg

1. Each of the first three laws of thermodynamics (zeroth, first, and second) leads to the existence of a state function.
   (a) List the state function from each law.
   (b) It is nice to have a molecular picture of the macroscopic thermodynamic state functions. Interpret the microscopic nature of these state functions. (20%)

2. 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
ρ/kg m^{-3}	0.225	0.456	0.664	1.062	1.468	1.734

3. 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
$C_{p,m}$/JK^{-1}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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4. Considering the dissociation reaction of dinitrogen tetroxide: $N_2O_4(g) \leftrightarrows 2NO_2(g)$, the Gibbs energy changes of formation N_2O_4 and NO_2 ($\Delta G_f°$) 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 $n_{N_2O_4} = 1-\xi$, and $n_{NO_2} = 2\xi$, 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:

$$-\frac{d[C_2H_6]}{dt} = k_{app}[C_2H_6]$$

Given the following possible elementary processes:

$C_2H_6 \rightarrow 2CH_3$	k_1
$CH_3 + C_2H_6 \rightarrow CH_4 + C_2H_5$	k_2
$C_2H_5 \rightarrow C_2H_4 + H$	k_3
$H + C_2H_6 \rightarrow C_2H_5 + H_2$	k_4
$H + C_2H_5 \rightarrow C_2H_6$	k_5

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,..... (20%)