第一部份 物理化學考題(50 分)

(I). 單選題 (選出一個最適當的答案): 每題 3 分，共 36 分. (答案直接填入 "選擇題作答區" 內)

1. Assuming that the atmosphere is isothermal at 0°C and that the average molar mass of air is 29 g mol^{-1}, what is the atmospheric pressure at 6100 m above sea level? (Choose the closest answer)
   (A) 0.1 atm (B) 0.25 atm (C) 0.5 atm (D) 0.8 atm (E) 1.0 atm
2. Which molecule has the largest van der Waals a constant?
   (A) H_2 (B) He (C) N_2 (D) O_2 (E) Cl_2
3. The enthalpy change for burning ketene (CH_2CO)
   $CH_2CO(g) + 2\ O_2(g) \longrightarrow 2\ CO_2(g) + H_2O(g)$
   is $\Delta H_1 = -981.1$ kJ at 25°C. The enthalpy change for burning methane
   $CH_4(g) + 2\ O_2(g) \longrightarrow CO_2(g) + 2\ H_2O(g)$
   is $\Delta H_2 = -802.3$ kJ at 25°C. What is the enthalpy change for the reaction below?
   $2\ CH_4(g) + 2\ O_2(g) \longrightarrow CH_2CO(g) + 3\ H_2O(g)$
   (A) -178.8 kJ (B) -623.5 kJ (C) 178.8 kJ (D) 623.5 kJ (E) None of the above
4. Estimate the heat evolved in freezing water at -10 °C using the following information:
   $H_2O(l) \rightarrow H_2O(s)$　　$\Delta H°(273K) = -6004$ J mol^{-1}
   $C_P(H_2O,l) = 76.3$ J K^{-1} mol^{-1}
   $C_P(H_2O,s) = 36.8$ J K^{-1} mol^{-1}
   (A) -5.6 kJ mol^{-1} (B) -5.8 kJ mol^{-1} (C) -6.0 kJ mol^{-1} (D) -6.2 kJ mol^{-1} (E) -6.4 kJ mol^{-1}
5. What is the change of entropy when a mole of isolated ideal gas initially at 298 K is expanded into a volume that is twice as large as its initial volume?
   (A) 16.63 J K^{-1} (B) 5.76 J K^{-1} (C) 0 J K^{-1} (D) -5.76 J K^{-1} (E) -16.63 J K^{-1}
6. Toluene is vaporized at its boiling point, 111°C. Given that the heat of vaporization of toluene at this temperature is 361.9 J g^{-1}. What is ΔG for the vaporization of toluene at 111°C?
   (A) -33.34 kJ mol^{-1} (B) -3.193 kJ mol^{-1} (C) 0.0 kJ mol^{-1} (D) 3.193 kJ mol^{-1} (E) 33.34 kJ mol^{-1}
7. Given $\hat{p}_x = -i\hbar\frac{d}{dx}$, what is the commutator $[\hat{p}_x, \hat{x}]$?
   (A) $-i\hbar$ (B) $i\hbar$ (C) $i\hbar\hat{p}_x$ (D) $-i\hbar\hat{p}_x$ (E) None of the above
8. Consider boron atom in the configuration [He]$2s^2 2p^1$. This configuration contains three terms: ^2P, ^2D, ^4S. The number of states that belong to the ^2D term is?
   (A) 2 (B) 4 (C) 6 (D) 10 (E) 20
9. How many Raman active modes are there in the linear acetylene (C_2H_2) molecule?
   (A) 4 (B) 3 (C) 2 (D) 1 (E) 0
10. Which one of the following statements is true?
    (A) The zero-point energy is higher for a Helium atom in a box than for an electron
    (B) When the quantum tunneling effect occurs, a particle instantaneously receive extra energy to overcome the energy barrier because of the uncertainty principle
    (C) The wavefunction of a system must satisfy the time-independent Schrodinger equation
    (D) If ϕ and ψ are both eigenfunctions of the linear operator A, then their linear combinations are also eigenfunctions of A.
    (E) For the n=8 harmonic oscillator energy state, the sign of the wavefunction in the right classical forbidden region is opposite the sign of it in the left classical forbidden region
11. Based on the conventional α/β spin functions, which spin function below is a singlet state?
    (A) $\alpha(1)\beta(2)$ (B) $2^{-1/2}[\alpha(1)\alpha(2) + \beta(1)\beta(2)]$ (C) $2^{-1/2}[\alpha(1)\alpha(2) - \beta(1)\beta(2)]$
    (D) $2^{-1/2}[\alpha(1)\beta(2) + \beta(1)\alpha(2)]$ (E) $2^{-1/2}[\alpha(1)\beta(2) - \beta(1)\alpha(2)]$
12. The order of the elementary reaction $2NO + O_2 \rightarrow 2NO_2$ is?
    (A) 0 (B) 1 (C) 2 (D) 3 (E) 4

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(II). 敘述與計算題 (共 14 分):

13. In Huckel theory, the Coulomb integral is α and the resonance integral is β.
(A) Sketch the Huckel molecular orbitals for both LUMOs of the benzene molecule. (2 points)
(B) What is the contribution to the stabilization of the electronic energy of ethylene due to the single π bond? What is the contribution for benzene (three conjugated bonds)? (2 points)
(C) Given that the heat of hydrogenation of cyclohexene is -121 kJ mol^{-1} and the heat of hydrogenation of benzene is -209 kJ mol^{-1}, calculate the value of β. (2 points)

14. Consider making diamonds from graphite:
C(graphite) → C(diamond)　$\Delta G° = 2.9$ kJ mol^{-1}
The densities of graphite and diamond may be taken to be 2.25 and 3.51 g cm^{-3}, respectively.
We further assume that the densities are independent of pressure.
(A) Show that $(\partial \Delta G/\partial P)_T = \Delta V$. ($G = E\text{-}TS$) (2 points)
(B) Calculate the equilibrium pressure for the conversion of graphite to diamond at 25°C. (2 points)

15. Consider the mechanism for the decomposition of NO_2Cl:

$$NO_2Cl \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} NO_2 + Cl$$

$$NO_2Cl + Cl \xrightarrow{k_2} NO_2 + Cl_2$$

Assuming that the second step is the rate determining step, determine the rate law of the overall reaction. (4 points)

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第二部份 **Analytical Chemistry (50%)**

(*Please write down your answer in detail*)

1. A new technique for determining glucose in serum is proposed by John and is compared to the established government method. Both methods are performed on serum from the same six patients in order to avoid patient-to-patient variability. Do the following data confirm a difference in these two methods at the 95% confidence level? (10%)

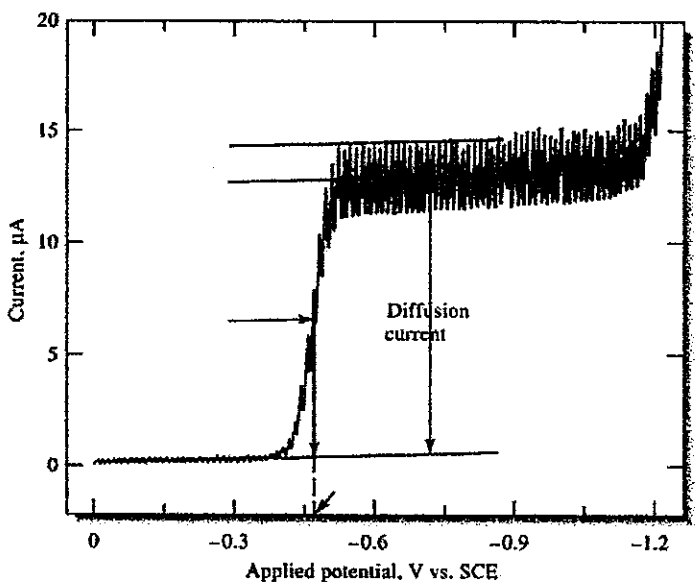
	Patient 1	Patient 2	Patient 3	Patient 4	Patient 5	Patient 6
John's method	1042	649	799	718	971	850
Government's method	1026	638	794	709	949	825

Values of *t* for Various Levels of Probability

Degrees of Freedom	80%	90%	95%	99%	99.9%
1	3.08	6.31	12.7	63.7	637
2	1.89	2.92	4.30	9.92	31.6
3	1.64	2.35	3.18	5.84	12.9
4	1.53	2.13	2.78	4.60	8.61
5	1.48	2.02	2.57	4.03	6.87
6	1.44	1.94	2.45	3.71	5.96
7	1.42	1.90	2.36	3.50	5.41
8	1.40	1.86	2.31	3.36	5.04
9	1.38	1.83	2.26	3.25	4.78
10	1.37	1.81	2.23	3.17	4.59
15	1.34	1.75	2.13	2.95	4.07
20	1.32	1.73	2.09	2.84	3.85
40	1.30	1.68	2.02	2.70	3.55
60	1.30	1.67	2.00	2.62	3.46
∞	1.28	1.64	1.96	2.58	3.29

2. Sarah plans to titrate 50.00 mL of 0.1000 M maleic acid, HOOC–CH=CH–COOH, with 0.1000 M NaOH. Please help her to calculate the pH value of the solution after introducing 50.15 mL of 0.1000 M NaOH. (10%)
(Maleic acid: $K_{a1} = 1.3 \times 10^{-2}$, $K_{a2} = 5.9 \times 10^{-7}$)

3. Eric found a piece of literature describing an experiment but most of the materials are lost on this paper. Base on the figure he found, shown below, please help him to describe what type of experiment it was, what kind of instrument was used, and how was the experiment conducted in this work. (10%)



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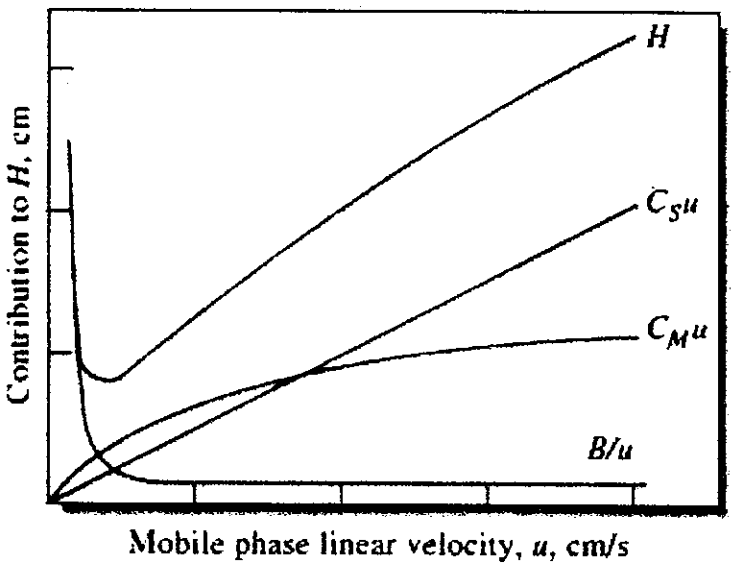
4. Mark found an analytical chemistry textbook and is interested in a figure, shown below, in the chromatography chapter. Please help him to understand the meaning of it by describing it in detail. (10%)



5. John, Sarah, Eric, and Mark are attending a chemistry course final exam. The instructor provides this figure to test if they can understand her lecture. If you were one of them, how could you interpretate this following figure? (10%)

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