國立臺灣大學 107 學年度碩士班招生考試試題

題號:202

202 科目: 物理化學(B)

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注意事項:

題號:

1. 請勿在答案本第一頁(制式表格)中作答。所有答案皆須寫在答案本第二頁之後。

2. 請標明題號,依序作答。

ln(5.00)=1.609; ln(2.00)=0.6931; ln(3.00)=1.099; 3. ln(1.00)=0.00; $\exp(1.00)=2.718$; $\exp(2.00)=7.389$; $\exp(3.00)=20.09$; $\exp(5.00)=148.4$

- 1. The exhaled volume of air can be measured by directing the air via a tube into the bottom of an apparatus to lift a piston against air and measuring the change in volume of the piston. If a patient under the measurement against the air of pressure 1.00 atm (101.0 kPa) gives a change in volume of 0.300 L, calculate the work in Pa-m³ and in kJ done by the patient in the measurement.
- 2. (a) Calculate the frequency in hertz and the wavenumber of a photon whose wavelength is $10.0 \mu m$. (b) When measured with a 1.00-cm cell, a 1.00x10⁻⁴ M solution of a sample exhibited absorbance of 0.500 at 540 nm. Calculate the molar absorptivity of (5%)the sample at 540 nm.
- 3. A change in a thermodynamic property must apply for a reaction that can be carried out by electrolysis. What are the property (2%)and its condition? Explain.
- 4. The following data were obtained for the gas-phase decomposition of nitrosyl chloride,

$$\begin{array}{lll} \text{2NOCl(g)} & \Longrightarrow & 2\text{NO(g)} + \text{Cl}_2(\text{g}) \\ & [\text{NOCl}]_0 & \text{Initial Rate} \\ & \underline{\text{(molecules/cm}^3)} & \underline{\text{(molecules/cm}^3-s)} \\ & 1.0\text{x}10^{16} & 7.0\text{x}10^3 \\ & 2.0\text{x}10^{16} & 2.7\text{x}10^4 \\ & 3.0\text{x}10^{16} & 6.0\text{x}10^4 \\ & 4.0\text{x}10^{16} & 1.1\text{x}10^5 \end{array}$$

Defining the rate as -Δ[NOCl]/Δt. (a) Write the rate law. (b) Calculate the value of the rate constant. (c) Calculate the value of the rate constant when concentrations are given in moles per liter. (7%)

- 5. For an electron in the lowest energy state of a hydrogen atom, its wavefunction is proportional to e^{-r/a_0} , with $a_0 = 52.9$ pm and r the distance from the nucleus. Here, for the sake of convenience in calculation, assume $a_0 = 50.0$ pm, instead, and calculate the ratio of the probability of finding the electron inside a small volume located at the nucleus (i.e., r = 0) to the probability at $r = a_0$ away from the nucleus. (5%)
- 6. For the reaction aA \longrightarrow products occurring at 25 °C and [A]₀ = 2.00x10⁻³ M, a plot of 1/[A] versus time based on the concentration versus time data collected for this reaction shows a straight line with a slope value of +1.00x10⁻² L/mol-s. (a) Determine the rate law, the integrated rate law, and the value of the rate constant for the reaction. (b) Determine the half-life for the reaction. (c) Calculate the time it takes for the concentration of A to decrease to 2.86x10⁻⁴ M? (8%)

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7. The activation energy of self-diffusion of free liquid water is 18.0 kJ/mole. (a) The value is higher than most solvents undergoing self-diffusion via pure diffusion-limited transport. Explain. (b) In ice, activation energy of self-diffusion of water molecules is ~57.0 kJ/mole. Discuss the causes, in the molecular level, of the large increase in activation energy in ice. (c) How high the water temperature has to be increased from 26.8 °C to cause the rate constant of the diffusion to increase by a factor of 2.80?

- 8. According to World Health Organization, N₂O is among the most effective and safe medicines needed in a health system. It has indisputable effects of analgesia and anxiolysis and is used especially in surgery and dentistry for its anaesthetic and pain reducing effects. For N₂O at 298 K: C_v=30.38 J/K-mol, C_p=38.70 J/mol-mol)
 - (a) (i) Give the systematic name and common name of N₂O. (ii) Calculate the number of moles of N₂O gas in a 5.00-L cylinder of N₂O which is at 10.0 atm at 200 K. (iii) If a container is evacuated and the gas in the cylinder is allowed to escape entirely into the evacuated container, which is kept at the constant pressure of 1.00 atm at 200 K during the escape, what volume of the container would the gas take up?
 - (b) Does N2O (at 0 K) or He (at 10 K) have the greater value of S? Explain.
 - (c) (i) Calculate ΔS_{surr} for the following decomposition reaction of $N_2O(g)$ at 26.8 $^{\circ}$ C and 1 atm. (ii) Will the reaction be spontaneous at the specified temperature and pressure? Explain.

$$2 N_2 O(g) \rightarrow 2 N_2(g) + O_2(g) \Delta H^0 = -163.2 \text{ kJ}$$

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- (d) Predict and explain the kinetic order of the decomposition reaction of N₂O(g) shown in (c) to occur on a hot platinum surface.
- (e) (i) Draw all the possible Lewis structures of N₂O. (ii) Define resonance structure. (iii) Indicate which structures you have drawn in (i) are canonical forms of N₂O. (iv) Assign formal charges to the structures you have drawn in (i). (v) Predict if any of the Lewis structures of N₂O you have drawn in (i) can be eliminated on the basis of formal charges. If yes, which are they? If no, explain. (vi) Experiments show that the bond lengths of N-N and N-O in N₂O are 1.12 Å and 1.19 Å, respectively. Is your prediction consistent with the experimental results? Explain.
- (f) By definition, H = U + PV. Calculate q, w, ΔU , and ΔH for the process in which 88.0 g of N_2O gas is cooled from 1400°C to 400°C at a constant pressure of 5.00 atm. (26%)
- 9. All true viruses contain nucleic acid—either DNA or RNA—and protein. The nucleic acid encodes the genetic information unique for each virus. Many viruses are enveloped by a protective protein coat called a capsid. The protein is synthesized by specific genes in the nucleic acid of the virus. In Jan. 2018, Rice University scientists reported in ACS Nano a development of programmable adeno-associated viruses by modifying one of three proteins that assemble into the capsid. By chipping away at the viral protein, they discovered a path toward virus-like, nanoscale devices that may be able to deliver drugs to cells.
 - (a) Write down the full name in English of DNA.
 - (b) Is DNA unwinding a chemical or physical change? Explain.
 - (c) A UV photon can mutate a strand of DNA. Calculate the energy of a mole of UV photons having a wavelength of 100.0 nm.
 - (d) Iodomethane CH₃I is a carcinogen, possibly due to its ability to react with the DNA strand. Results of a kinetics experiment on the reaction is shown below:

[DNA] ₀	$[\mathrm{CH_3I}]_0$	Initial Rate
(µmol/L)	(µmol/L)	(µmol/L-s)
0.0500	0.0500	1.25x10 ⁻³
0.0500	0.1000	2.50x10 ⁻³
0.1000	0.1000	5.00x10 ⁻³

Derive the rate law to show which of the following could be a possible mechanism for the reaction.

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Mechanism A:

 $DNA + CH_3I \rightarrow DNA-CH_3^+ + I^-$

Mechanism B:

 $CH_3I \rightarrow CH_3^+ + I^-$ (slow)

 $DNA + CH_3^+ \rightarrow DNA - CH_3^+$ (fast)

(e) (i) Define entropy. (ii) Use the concept of entropy to explain why human DNA contains much more information as is needed to control the production of all the substances in the body.

- (f) Scientists now realize that maximizing entropy in one part of a system could induce organization (called entropic ordering) in another part of the system. For example, entropic forces may have caused the clustering of DNA in cells without nuclei. Use the concept of entropy to (i) discuss the conditions for entropic ordering to occur, and (ii) explain how entropic ordering could be important in the binding of proteins to form capsid.
- (g) Some cis complexes of platinum, such as cisplatin (cis-[PtCl₂(NH₃)₂]), show significant antitumor activity because of their interference with DNA replication, which kills the fastest proliferating cells, such as tumor cells. (i) Draw the structural formula for cis-[PtCl₂(NH₃)₂]. (ii) Give the systematic name for cis-[PtCl₂(NH₃)₂]. (iii) The trans stereoisomer of cisplatin is transplatin, which has no effect on tumors. Discuss what the localized electron model and crystal field model are and discuss if the localized electron model, crystal field model, or neither of them can explain the difference in antitumor activity between cisplatin and transplatin. (iv) Distinguish geometrical isomerism and optical isomerism. Do cisplatin and transplatin belong to geometrical isomerism or optical isomerism? (v) Geometrical isomerism and optical isomerism belong to stereoisomerism, which is one of the two main types of isomerism. Name the other type of isomerism and its subclasses.
- (h) (i) List the types of bond, based on electron sharing, possibly present within a molecule. (ii) List the types of intermolecular force that may cause the aggregation of the components of a substance in a condensed state. (iii) Discuss to distinguish the different forces listed in (ii) and arrange them in the order of increasing strength. (iv) Name all the types of bonds/forces that are involved in the synthesis of proteins using the genetic information stored in DNA. (v) Name all the possible types of forces associated with the drug which may be delivered to cells via the nanoscale devices mentioned above? (35%)

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