國立彰化師範大學 102 學年度碩士班招生考試試題

系所：化學系　　科目：物理化學

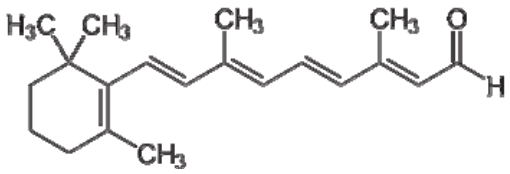
☆☆請在答案紙上作答☆☆　　

1. Given the equation of state of the ideal gas, PV = nRT, derive the following properties: (1) the isothermal compressibility factor, $\kappa_T = -(1/V)(\partial V/\partial P)_T$, (2) the Joule-Thomson coefficient, $\mu = (\partial T/\partial P)_H$, (3) $(\partial C_v/\partial V)_T$, (4) the adiabatic reversible work from an initial state (P_1 V_1) to a final state (P_2 V_2), given that $\gamma = C_{p,m}/C_{v,m}$. Express your answers in terms of P, V, n, T, γ or any numerical values. (20%)

2. Answer the following questions: (1) Given that ΔH^o_f for $H_2O(g)$, H(g) and O(g) are -241.8, 218.0 and 249.2 kJ mol^{-1}, respectively. Calculate the ΔU^o for the reaction $H_2O(g) \rightarrow 2H(g) + O(g)$. (2) Given that the molar combustion heat of CO at 450℃ is -285.85 kJ mol^{-1}. When 1.0 mole of CO is used as the fuel for a Carnot engine operating at between temperatures of 450℃ and 100℃, how much work can be generated by the engine? (3) Given that the density of the ice is 0.917 g cm^{-3}. When the pressure of ice at 0℃ is increased from 1.0 bar to 2.0 bar, how much will its chemical potential be changed? (4) Calculate the molar Gibbs energy of mixing for mixing benzene and toluene to form a most stable 2-components solution mixture at 298 K. (20%)

3. For a gas phase reaction, $2A(g) \rightarrow B(g)$, its rate constant (in sec^{-1}) and reaction temperature (in K) have the following relationship: $\ln k = 20 - 9000/T$. (1) What is the total reaction order for the reaction? Explain how you obtain the answer. (3%) (2) What is the value for the pre-exponential factor (in sec^{-1})? (3%) (3) What is the half -life of the reaction (in min.) at 27℃? (4%)

4. Retinal is a precursor to the pigment in the retina responsible for vision. The conjugated system of retinal consists of eleven C atoms and one O atom and the energy level of the retinal can be approximated by a particle in a box model. In the ground state of retinal, each level up to n=6 is fully occupied and has an average internuclear distance of 140 pm. Calculate (1) the energy separation between the ground state and the first excited state in which one electron occupies the state with n=7. (2) the frequency of the radiation required to produce a transition between these two states. h = 6.62608×10^{-34} Js(10 %)



The structure of retinal

5. Based on Arrhenius equation, the rate constant (k_r) for chemical reaction A+B→C can be approximated by

   $k_r = A \times e^{-E_a/RT}$,　A: pre-exponential factor　E_a: activation energy

   The concentration of A and B is [A] and [B]; The radius of A and B is equal to r_A and r_B; The mass of A and B is equal to M_A and M_B; The relative mean speed ($\overline{v_{rel}}$) $= \sqrt{\frac{8kT}{\pi\mu}}, \mu = \frac{M_A M_B}{M_A + M_B}$; Avogadro's constant is N_A. Please answer the following questions: (1) What is the collision frequency between A and B? (2) what is the temperature dependence of collision frequency? (3) can we use the temperature dependence of collision frequency to explain the temperature dependence of Arrhenius equation? (15 %)

6. For a consecutive unimolecular reaction

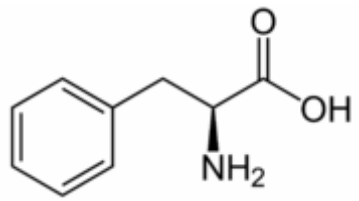
   $A \xrightarrow{k_a} B \xrightarrow{k_b} C$

   (1) Please write down the differential rate law of [A], [B] and [C], given that at time-zero $[A]=[A]_0$, $[B]_0=0$, $[C]_0=0$. Please draw the plots for [B] vs. time when (2) $k_a >> k_b$ (3)$k_a << k_b$. (15 %)

7. Phenylalanine is a naturally occurring amino acid. Assuming the interaction between phenyl group and peptide is the dipole-induced dipole interaction. *Please calculate the energy of interaction between its phenyl group and the electric dipole moment of a neighboring peptide group* (please express your answer in terms of J/mole). The dipole-induced dipole interaction energy (E):

   $$E = -\frac{C}{r^6}, C = \frac{\mu_A^{\ 2}\alpha_B}{4\pi\varepsilon_0}$$

   Where r is the separation between molecule A (with dipole moment=μ_A) and polarizable molecule B (with polarizability volume=α_B), ε_0 is the vacuum permittivity= 8.385419×10^{-12} J^{-1} C^2 m^{-1}. The distance between the phenyl group and peptide group is 4.0 nm, the dipole moment of the peptide group is 2.7 D (1D= 3.33564×10^{-30} C m) and the polarizability volume of phenyl group is 1.04×10^{-29} m^3 .(10%)



The structure of phenylalanine