國立交通大學 100 學年度碩士班考試入學試題

科目：物理化學(4073)(4061)　　　　　　　考試日期：100 年 2 月 18 日　第 1 節
系所班別：應用化學系分子科學碩士班、應化系甲組、　　　　　第 1 頁, 共 3 頁
【不可使用計算機】＊作答前請先核對試題、答案卷(試卷)與准考證之所組別與考科是否相符！！

1. (6 %) Derive the changes of internal energy (ΔU) and enthalpy (ΔH) for 1.0 mole of monatomic gas to decrease its temperature from T_1 to T_2 under (a) isobaric (constant pressure), (b) isochoric (constant volume), and (c) adiabatic (no heat transfer) conditions. Assuming that the gas behalves ideally and its heat capacitances are independence of temperature. Express your answer in terms of T_1, T_2 and R only. (2 % each)

2. (8 %) There are some possibilities that you may observe super-cooled water below 0 °C in the arctic area where the weather is extremely cold. Consider the super-cooled water at -10 °C to form ice at the same temperature, the molar entropy change of the system can be estimated as follows,

$$\Delta S = C_{p,m}^{water} \, ln\frac{T_m}{T} + \frac{\Delta H_{fus}}{T_m} + C_{p,m}^{ice} \, ln\frac{T}{T_m}$$

$$= 75.3 \times ln\frac{273}{263} + \frac{(-6010)}{273} + 37.7 \times ln\frac{263}{273} = -20.6 \, J \, K^{-1} mol^{-1} \; < 0$$

Your intuition tells you that the super-cooled water will freeze eventually, so this process should be spontaneous. Explain (a) why the change of entropy is negative but the process is spontaneous (against the 2nd law of thermodynamics?) (6 %), and (b) why you have the chance to observe the super-cooled water in the arctic area? (2 %)

3. (20 %) Chemical energy can be converted to do non-expansion work more efficiently than a heat engine to do the PV work. Here are our examples: you wish to construct a fuel cell to do electrical work, and a heat engine to do the PV work, based on the combustion of methane: (4 % each)

CH$_4$(g) + 2 O$_2$(g) → CO$_2$(g) + 2 H$_2$O(l)　　　　　　ΔH_c^0 = -891 kJ mol^{-1}
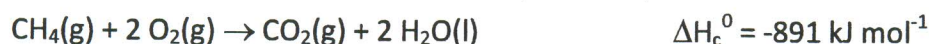
(a) Giving that the standard entropy of the reaction ΔS_r^0 = -243 J K^{-1}mol^{-1}, estimate the minimum heat that must be released to the environment which cannot be transferred to do work at 300 K and 1 bar.

(b) Estimate the maximum PV (expansion) work available through the combustion of one mole methane in the fuel cell at 300 K and 1 bar.

(c) Estimate the maximum electrical (non-expansion) work available through the combustion of one mole methane in the fuel cell at 300 K and 1 bar.

(d) If a reversible heat engine is operating between 300 and 600 K, estimate the maximum efficiency available for this engine.

(e) If the heat generated by the combustion of one mole methane at the standard-state condition is used to boost the heat engine, estimate the maximum PV work that can be done by the engine.

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4. (16 %) For a multiple component system, the differential form of the Gibbs free energy is given by $dG = -SdT + VdP + \sum_i \mu_i dn_i$, answer the following questions accordingly. (4 % each)

(a) If μ_1^{vapor} can be expressed as $\mu_1^0 + RT\,ln\,(P_1/1\,bar)$ for component 1 and P_1 represents the vapor pressure of component 1, give the physical meaning for μ_1^0.

(b) If Raoult's law is followed for component 1 as the mole fraction $x_1 \to 1$, its chemical potential may be derived as $\mu_1^{soln} = \mu_1^*(RL) + RT\ln x_1$. Determine $\mu_1^*(RL)$ in terms of μ_1^0, vapor pressure, and temperature. Assume ideal vapor and ideal solution.

(c) If Henry's law is followed for component 2 as $x_2 \to 0$, the standard state must be re-defined with an artificial vapor pressure. Now its chemical potential may be derived as $\mu_2^{soln} = \mu_2^*(HL) + RT\ln x_2$. Determine $\mu_2^*(HL)$ in terms of μ_2^0, vapor pressure (artificial), and temperature. Assume ideal vapor and ideal solution.

(d) If one assumes $x_2 \to 1$ in order to express μ_2^0 in terms of $\mu_2^*(HL)$, pressure and temperature. In this way you will obtain the relationship between the two standard states, i.e., $\mu_2^*(HL) = \mu_2^*(RL) + RT\,ln\,\omega$, determine ω in terms of vapor pressures.

5. (10 %) Consider a particle of mass m in a one-dimensional box of length a. Its average energy is given by
$$\langle E \rangle = \frac{1}{2m}\langle p^2 \rangle$$
Because $<p> = 0$, $<p^2> = \sigma_p^2$, where σ_p can be called the uncertainty in p. Using the Uncertainty Principle, show that the energy must be at least as $\hbar^2/8ma^2$ because σ_x, the uncertainty in x cannot be larger than a.

6. (10 %) Consider the Bohr frequency condition $\Delta E = h\nu$ for this problem. The frequencies at which the absorption transitions occur are $\nu = 2B(J+1)$ $J = 0,1,2,...,$ where $B = \dfrac{h}{8\pi^2 I}$ is the rotational constant of the molecule, ν is the frequency of the electromagnetic radiation, J is the rotational quantum number, the moment of inertia I is $I = \mu r^2$. To a good approximation, the microwave spectrum of compound XY consists of a series of equally spaced lines, separated by 3.31×10^{11} Hz. Estimate the bond length of X-Y by using masses of X (1.00 amu) and Y (3.05 amu), and the following values: Planck constant $h = 6.62 \times 10^{-34}$, a 1 amu = 1.66×10^{-27} kg, $1/\pi = 0.32$, $1/\pi^2 = 0.10$.

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7. (12 %) Using MO theory for benzene molecule, consider the following questions:

   (a) Write down the wavefunctions for the π molecular orbitals of benzene. (4 %)

   (b) Draw the energy diagram of benzene with corresponding energies. (4 %)

   (c) Draw the π molecular orbitals for benzene and indicate the nodal planes. (4%)

8. (6 %) There are species derived from oxygen molecule, such as O_2^+, O_2, O_2^-, O_2^{2-}, consider the following questions based on MO theory:

   (a) Write down the electronic configurations and bond orders of each species. (4 %)

   (b) Arrange the species in order of increasing bond length. (2 %)

9. (12 %) The rate of excited-state population change on spontaneous emission and stimulated emission are described with

$$-\frac{dN_2(t)}{dt} = A_{21}N_2(t) \tag{1}$$

$$-\frac{dN_1(t)}{dt} = \frac{dN_2(t)}{dt} = B_{12}\rho_{12}(\nu_{12})N_1(t)' \tag{2}$$

Here, A_{21} and B_{12} are Einstein coefficients, ρ is the radiant energy density ($J \cdot m^{-3} \cdot s$), ν_{12} is the frequency of the electromagnetic radiation (cm^{-1}), and N_1 and N_2 are the number of atoms in ground and excited states, respectively.

The equilibrium spectral radiant energy density $\rho(\nu_{12})$ is explained following two equations;

$$\rho_v(\nu_{12}) = \frac{8\pi h}{c^3} \frac{\nu_{12}^3}{\exp(h\nu_{12}/k_B T) - 1} \tag{3}$$

$$\rho_v(\nu_{12}) = \frac{A_{21}}{B_{12}\exp(h\nu_{12}/k_B T) - B_{21}} \tag{4}$$

h is the Planck constant (6.62×10^{-34} J·s), c is the velocity of light (3.0×10^8 m·s^{-1}), k_B is the Boltzmann constant (1.38×10^{-23} J·K^{-1}), T is the temperature. Answer the following questions:

   (a) What are the units of Einstein coefficients A_{21} and B_{12}, respectively? (2 %)

   (b) Prove that equations (3) and (4) are equivalent only if $B_{12} = B_{21}$, and $A_{21} = (8\pi h \nu_{12}^3/c^3)B_{12}$. (10 %)