國立台灣科技大學九十六學年度碩士班招生試題

系所組別： 高分子工程系碩士班丁組

科　　目： 物理化學

共 10 大題，總分 100 分；請於答案卷內依序作答。

1. What is the "Carnot cycle"? Can you plot this "Carnot cycle" in P-V diagram? Express operating conditions, like isothermal or adiabatically, for each process. What is the definition of "Efficiency"? Can you show the efficiency of Carnot cycle in "Temperature". (20%)

2. Determine the reaction heat of the following reaction at temperature T K,

$$M_{(l)} + 1/2O_{2(g)} = MO_{(l)}$$

where the reaction temperature T comparing with melting points of $T_{m,Mo}$ and $T_{m,M}$ is like $T > Tm,_{MO} > Tm,_{M}$

Illustrate the diagram of relationship of H and T, then explain each reaction process.(10%) PS: You can assume or define any thermodynamics properties in this question for answering this question.

3. One mole of an ideal gas at 300K is isothermally compressed from a volume of 25.0 L to a volume of 10.0 L by a constant external pressure. At the end of the process, $P=P_{external}$. Because $P \neq P_{external}$ at all but the final state, this process is irreversible. The temperature of the surroundings is 300K. Calculate (a)ΔS (4%), (b)$\Delta S_{surroundings}$ (4%), and ΔS_{total} (2%).

4. At 298K, the thermal expansion coefficient and the isothermal compressibility of liquid water are $\beta=2.04\times10^{-4}K^{-1}$ and $\kappa=45.9\times10^{-6}$ bar^{-1}.

(a)Calculate $\left(\frac{\partial U}{\partial V}\right)_T$ for water at 320K and P=1.00 bar. (4%)

(b)If an external pressure equal to $\left(\frac{\partial U}{\partial V}\right)_T$ were applied to 1.00 m3 of liquid water at 320 K, how much would its volume change? What is the relative change in volume? (4%)

(c)Calculate $\left(\frac{\partial U_m}{\partial V}\right)_T$ for $N_2(g)$ at 320 K and P=1.00 atm given that a=1.35 $atmL^2mol^{-2}$ using $\left(\frac{\partial U_m}{\partial V}\right)_T = \frac{a}{V_m^2}$ for a van der gas. Compare the value that you obtain with that of part (a) and discuss the difference. (4%)

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5. An ideal solution is made from 5.00 mol of benzene and 3.25 mol of toluene. At 298K, the vapor pressure of pure substances $P^*_{benzene}$=96.4 Torr and $P^*_{toluene}$=28.9 Torr.
(a)The pressure above this solution is reduced from 760 torr. At what pressure does the vapor phase first appear? (4%)
(b)What is the composition of the vapor under these conditions? (4%)

6. (8%) At 413 K, a solution of liquid ethanol (mole fraction= 0.9006, saturated vapor pressure= 130.4 torr) and isooctane (saturated vapor pressure= 43.9 torr) forms a vapor phase with a mole fraction of ethanol in vapor equal to 0.6667 at a total gas pressure of 185.9 torr.
(a) Find the fugacity for both gaseous and liquid isooctane components. Also give the assumption(s) to reach the results.
(b) Calculate the activity and activity coefficient of ethanol in solution.
(c) Find the Gibbs free energy of mixing at this temperature and mixing ratio. (gas constant= 8.314 $J(K\text{- }mol)^{-1}$)

7. (8%) The densities of pure water and ethanol are 997 and 789 kg/m^3, respectively. The partial molar volumes of ethanol and water in a solution with mole fraction of ethanol in liquid equal to 0.20 are 55.2 and 17.8 cm^3/mol, respectively.

(a) Find the molar volume of this solution with the given mixing ratio.
(b) While 2 moles of ethanol is mixed with 8 moles of water, find the change in volume relative to the pure components.
(c) From the results in (b), what can you conclude regarding the intermolecular forces in the mixture versus in the pure components?

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8. (8%) "The particle in a well" is an approximate model to describe the absorption of visible light in a conjugated molecule. Consider the butadiene and four delocalized electrons in two pi-orbitals of this molecule:

(a) The light is absorbed by the molecule, leading to the transition of an electron from the ground level (quantum number= 2) to the excited (quantum number= 3). Find the energy of transition for an electron. (Given: the length of butadiene= 5.78 Angstroms; mass of electron= $9.11X10^{-31}$ kg; Planck constant= $6.626X10^{-34}$ J-s)

(b) Find the wavelength of radiation.

(c) Another more rigorous approach to find the energy of electron transition in conjugated molecules is Huckel molecular orbital theory. Explain its difference with the particle-in-well model.

9. (8%) The theoretical basis for the P-T phase diagram in a pure substance is Clapeyron equation that relates the equilibrium pressure with temperature during phase transition.

(a) Use the first and the second laws of thermodynamics to derive the Clapeyron equation.

(b) For the fusion transition, the slope of the solid-liquid coexistence curve is positive for all solids, except ice. Why so?

(c) Sketch schematically the phase diagram for all materials excluding water, and also indicate the solid-phase regime, critical point, and triple point.

10. (8%) The "simple harmonic oscillator" is an approximate model to describe the vibrational levels of a diatomic molecule.

(a) The vibration frequency of the $^{14}N_2$ molecule corresponds to a wave number of 2360 cm^{-1}. What is the lowest vibration energy? (light speed= 3.00×10^8 m/s)

(b) Predict the wave number of $^{15}N^{14}N$ molecule, from the above information.

(c) The observation of photons emitted when molecules make transitions between different vibrational levels is an important source of information on interatomic forces. How can you quantify the interatomic forces in diatomic molecules with vibration frequencies?