國立高雄大學 103 學年度研究所碩士班招生考試試題

科目：綜合化學(II)　　系所：應用化學系　　是否使用計算機：是

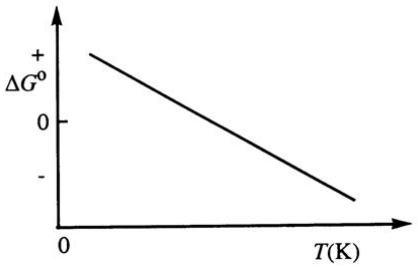
考試時間：100 分鐘　　本科原始成績：100 分

常數：R = 8.314 J K^{-1} mol^{-1}, $k = 1.38\times10^{-23}$ J K^{-1}, $h = 6.626\times10^{-34}$ J s. 公式: $\frac{kT}{\sigma hcB}, \frac{V}{\Lambda^3}, \frac{1}{1-e^{-hc\bar{\upsilon}/kT}}$

I. 選擇題: (18%, 每題 2 分)

1. A sample consisting of 1.00 mol of perfect gas atoms, for which $C_{V,m}$ = 7/2R, initially at p = 1.00 bar and T_1 = 273 K, is heated reversibly to 373 K at constant volume. Calculate the work, w , in kJ. (A) +2.91 kJ (B) -2.91 kJ (C) +3.74 kJ (D) -3.74 kJ (E) None of these choices.

2. Consider the figure below which shows ΔG° for a chemical process plotted against absolute temperature. From this plot, it is reasonable to conclude that: (A) ΔH° > 0, ΔS° > 0 (B) ΔH° > 0, ΔS° < 0 (C) ΔH° < 0, ΔS° > 0 (D) ΔH° < 0, ΔS° < 0 (E) None of these choices.



3. The second law of thermodynamics tells us that

   (A) the entropy of the universe is constant. (B) entropy is neither created nor destroyed.

   (C) the universe proceeds towards a state of lower entropy. (D) the universe proceeds towards a state of higher entropy. (E) the universe cannot create entropy.

4. Calculate E°cell and indicate whether the overall reaction shown is spontaneous or nonspontaneous.

   $H_2O_2(aq) + 2H^+(aq) + 2e^- \rightleftharpoons 2H_2O(l)$ $E° = 1.77$ V
   $Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$ $E° = 0.77$ V

   Overall reaction: $2Fe^{3+}(aq) + 2H_2O(l) \rightarrow H_2O_2(aq) + 2H^+(aq) + 2Fe^{2+}(aq)$

   (A) $E°_{cell}$ = -1.00 V, nonspontaneous (B) $E°_{cell}$ = -1.00 V, spontaneous (C) $E°_{cell}$ = 1.00 V, nonspontaneous (D) $E°_{cell}$ = 1.00 V, spontaneous (E) $E°_{cell}$ = -0.23 V, nonspontaneous.

5. An ideal solution is made up of the volatile liquids A and B, for which P_A^* = 172 Torr (the vapor pressure of pure A) and P_B^* = 57.6 Torr (the vapor pressure of pure B). As the pressure is reduced, the first vapor is observed at a total pressure of 70.0 Torr. What is x_A (the mole fraction of A in the liquid)? (A) 0.032 (B) 0.045 (C) 0.108 (D) 0.345 (E) 0.645

6. At the transition temperature of 368 K, the enthalpy of transition from rhombic to monoclinic sulfur is 380 J mol^{-1}. Calculate the entropy of transition under these conditions? (A) 0.96 J $K^{-1}mol^{-1}$ (B) 1.03 J $K^{-1}mol^{-1}$ (C) 1.96 J $K^{-1}mol^{-1}$ (D) 2.34 J $K^{-1}mol^{-1}$ (E) None of these choices.

7. One mole of an ideal gas at 300 K is reversibly and isothermally compressed from a volume of 25.0 L to a volume of 10.0 L. Because it is very large, the temperature of the water bath thermal reservoir in the surroundings remains essentially constant at 300 K during the process. Calculate the entropy change of the universe; ΔS_{univ} ? (A) 7.62 J K^{-1} (B) 14.5 J K^{-1} (C) 24.5 J K^{-1} (D) -7.62 J K^{-1} (E) 0 J K^{-1}.

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8. A sample containing 1.0 mol of He (1 bar), 3.0 mol of Ne (1 bar), 2.0 mol of Ar (1 bar) and 2.5 mol of Xe (1 bar), all at 298 K. The value of ΔG_{mixing} is the -27.81 kJ. What is the value of ΔS_{mixing}? (A) -93.3 J K^{-1} (B) 93.3 J K^{-1} (C) -0.093 J K^{-1} (D) 0.093 J K^{-1} (E) 0 J K^{-1}.
9. Consider the following quantities used in thermodynamics: U (internal energy), H (enthalpy), q (heat), w (work), S (entropy), G (Gibbs free energy). How many of them are state functions? (A) 0 (B) 2 (C) 3 (D) 4 (E) None of these choices.

II. 簡答題：(32%, 每題 8 分)

10. The energy eigenvalues for the particle in a one-dimensional box are: $E_n = \frac{h^2 n^2}{8ma^2}$, where n, E_n, h, m, and a are the quantum number, energy eigenvalue at the level n, Planck's constant, the mass of the particle, and the length of the one dimensional box, respectively. (a) Plot the first four eigenfunctions for the particle in a box and shown together with the corresponding energy eigenvalues as a function of the portion of a (x/a). (b) Plot the probability density as a function of x/a.
11. The following two hybrid orbitals describe two localized bonds of H_2O. Prove that these two hybrid orbitals are (a) normalized, and (b) orthogonal to each other.

    $\Psi_a = 0.55\square_{2pz} + 0.71\square_{2px} - 0.45\square_{2s}$, and $\Psi_b = 0.55\square_{2pz} - 0.71\square_{2px} - 0.45\square_{2s}$,
12. Calculate (a) translational, (b) rotational , and (c) vibrational partition functions of 1 mole I_2 at 300 K and 1 atm. Molecular parameters of I_2 include the thermal wavelength 6.33 pm, rotational constant 0.03735 cm^{-1}, and vibrational constant 208 cm^{-1}. (You don't have to calculate the answer for (c). Writing down the right equation with right numbers in it is sufficient.)
13. A sequential first-order reactions A → I (k_A) and I→ P (k_I). (a) Write down the differential rate expressions for d[A]/dt, d[I]/dt, and d[P]/dt. (b) For what kind of sequential reactions can one apply the steady-state approximation to solve the rate equations? (c) What is [I] under such steady-state conditions.

III. 計算題：(25%, 每題 5 分)

14. Find the molarity (M) of 20.0 wt% HX (aq). The density of HX (aq) is 1.2 g/mL and the molecular mass of HX is 24.0 g/mol.
15. A solution contained a weak acid (HA) and its conjugate base (A^-). The relative ratio of concentration $[A^-]/[HA]$ is 1 and the pH of the solution is 6. Find the pK_a of the HA.
16. K_a for weak acid HA is 1×10^{-5}. Find K_b for A^-.

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17. Calculate the activity coefficient of Fe^{3+} in a solution of 0.2 mM $Fe_2(SO_4)_3$.
18. Consider the titration of 50.0 mL of 0.02 M weak acid (HA) with 0.02 M NaOH. Calculate the pH at the titration equivalence point. (K_b for weak acid HA is 1×10^{-6})

IV. 簡答題：(25%, 每題 5 分)

19. Explain why the pH of 10^{-9} M KOH (*aq*) is approximately 7.
20. Describe how to perform the standard addition technique for quantitative analysis.
21. Explain the difference between fluorescence and phosphorescence.
22. Why bands of solute will spread (broaden) in HPLC chromatogram?
23. List the sources of error associated with pH measurement using the glass electrode.

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