

# 國立中央大學八十七學年度碩士班研究生入學試題卷

所別: 化學研究所 不分組 科目: 物化·分析 共2頁 第1頁

## 分析部份

1. In a series of experiments on the determination of tin in foodstuffs, samples were boiled with hydrochloric acid under reflux for different times. The results are shown below:

Refluxing time (min)	Tin found (mg/kg)
30	55, 57, 59, 56, 56, 59
75	53, 60, 58, 59, 55, 59

- (a) what are the 95% confidence limits of these two different refluxing times? ( $t=2.57$ ), and (b) test whether the variability of the results is greater for the longer boiling time (F-test,  $P=0.05$ ). (10 pts)
2. List the differences in properties and the roles of the mobile phases in gas chromatography (GC), liquid chromatography (LC), and supercritical-fluid chromatography (SFC). And explain how do these differences influence the characteristics of the three methods? (10 pts)
3. Iodimetry is one of the commonly used methods in potentiometric titration. The oxide of As(III),  $H_3AsO_3$ , can be used to standardize triiodide  $I_3^-$  solutions, prepared by dissolving  $I_2$  crystals in KI solution. Given the standard reduction potentials of 0.54 V for  $I_3^-/I^-$  and 0.56 V for  $H_3AsO_4/H_3AsO_3$ , answer the following questions.
- (a) What is the equilibrium constant of the redox reaction  $I_3^- + H_3AsO_3 \rightarrow I^- + H_3AsO_4$  (unbalanced)? Is this a thermodynamically favorable reaction?
- (b) How does pH of the solutions affect the redox reaction in (a)? Under what conditions should the titration be performed?
- (c) Draw a titration curve of this system to illustrate how the potential is changed by the amount of 0.1 M  $I_3^-$  titrant added to a 50 mL aliquot of 0.1 M  $H_3AsO_3$  standard solution whose pH was buffered at 9. Calculate the potential at the equivalent point. (10 pts)
4. (a) Calculate the pH of a buffer solution prepared by adding 20 mL of 0.10 M acetic acid to 20 mL of 0.10M sodium acetate. (dissociation constant of acetic acid =  $1.7 \times 10^{-5}$ )
- (b) The change of pH of the solution in (a) after a 1 mL of 0.1 M HCl solution was added.
- (c) The change of pH of solution in (a) after 1 mL of 0.1 M NaOH solution was added. (10 pts)
5. Define the following terms. (10 pts)
- (a) calomel reference electrode
- (b) linear sweep cyclic voltammetry
- (c) Beer's Law
- (d) Van Deemter equation
- (e) Zeeman background correction

Table A.2 - Critical values of F for a one-tailed test ( $P = 0.05$ )

$v_1 \backslash v_2$	1	2	3	4	5	6	7	8	9	10	12	15	20
1	161.4	199.5	215.7	224.6	230.2	234.0	236.8	238.9	240.5	241.9	243.9	245.9	248.0
2	18.51	19.00	19.16	19.25	19.30	19.33	19.35	19.37	19.38	19.40	19.41	19.43	19.45
3	10.13	9.552	9.277	9.117	9.013	8.941	8.887	8.845	8.812	8.786	8.745	8.703	8.660
4	7.709	6.944	6.591	6.388	6.256	6.163	6.094	6.041	5.999	5.964	5.912	5.859	5.803
5	6.608	5.786	5.409	5.192	5.050	4.950	4.876	4.818	4.772	4.731	4.678	4.619	4.558
6	5.987	5.143	4.757	4.534	4.387	4.284	4.207	4.147	4.099	4.060	4.000	3.938	3.874
7	5.591	4.717	4.347	4.120	3.972	3.866	3.787	3.726	3.677	3.637	3.575	3.511	3.445
8	5.318	4.459	4.066	3.838	3.687	3.581	3.500	3.438	3.388	3.347	3.284	3.218	3.150
9	5.117	4.256	3.863	3.633	3.482	3.374	3.293	3.230	3.179	3.137	3.073	3.006	2.936
10	4.965	4.103	3.708	3.478	3.326	3.217	3.135	3.072	3.020	2.978	2.913	2.845	2.774
11	4.844	3.982	3.587	3.357	3.204	3.095	3.012	2.948	2.896	2.854	2.788	2.719	2.646
12	4.747	3.885	3.490	3.259	3.106	2.996	2.913	2.849	2.796	2.754	2.688	2.619	2.544
13	4.667	3.806	3.411	3.179	3.025	2.915	2.832	2.767	2.714	2.672	2.606	2.537	2.461
14	4.600	3.739	3.344	3.112	2.958	2.848	2.764	2.699	2.646	2.604	2.538	2.469	2.392
15	4.543	3.682	3.287	3.055	2.901	2.790	2.707	2.641	2.588	2.546	2.480	2.411	2.334
16	4.494	3.634	3.239	3.007	2.852	2.741	2.657	2.591	2.538	2.494	2.428	2.359	2.281
17	4.451	3.592	3.197	2.965	2.810	2.699	2.614	2.548	2.494	2.450	2.384	2.315	2.237
18	4.414	3.555	3.160	2.928	2.773	2.661	2.576	2.510	2.456	2.412	2.346	2.277	2.199
19	4.381	3.522	3.127	2.895	2.740	2.628	2.543	2.477	2.423	2.378	2.312	2.243	2.165
20	4.351	3.493	3.098	2.866	2.711	2.599	2.514	2.447	2.393	2.348	2.282	2.213	2.135

$v_1$  = number of degrees of freedom of the numerator and  $v_2$  = number of degrees of freedom of the denominator.

分析

注意：背面有試題

## 物化部份

6. (10%) Find the molar entropy change when  $H_2O$  at 1 atm and  $300^\circ K$  is taken to  $H_2O(g)$  at 1 atm and  $500^\circ K$ . The molar heat capacities are

$$\frac{C_p(H_2O(l))}{R} = 1.26 - 1.943 \times 10^{-2} T + 3.042 \times 10^{-3} T^2$$

$$\frac{C_p(H_2O(g))}{R} = 3.633 + 1.1951 \times 10^{-3} T + 1.34 \times 10^{-7} T^2$$

Also the heat of vaporization at  $T = 373.15^\circ K$  is 13.10 R.

7. (10%)  $XeF_2$  is a volatile solid near room temperature. The concentration of  $XeF_2(g)$  is directly proportional to the quantity call optical density. We have found O.D. to be 10 at 294K, and 1.2 at 267K. Determine the change in Gibbs Free energy and the enthalpy of sublimation of  $XeF_2$ .

8. (10%) In the following table are listed specific rate constants ; k, for the decomposition  $N_2O_5$  at various temperatures:

$t(^{\circ}C)$	$k(sec)^{-1}$
0	$7.87 \times 10^{-7}$
25	$3.46 \times 10^{-5}$
35	$1.35 \times 10^{-4}$
45	$4.98 \times 10^{-4}$
55	$1.50 \times 10^{-3}$
65	$4.87 \times 10^{-3}$

Determine the energy of activation, and find the specific rate constant at  $50^\circ C$ .

9. (10%) For a one dimensional harmonic oscillator, find the average energy  $\langle E \rangle$ ,  $\langle E^2 \rangle$  and the deviation of energy  $\sigma_E$  if the state just prior to the measurement is the state corresponding to the normalized wave functions  $\psi = \frac{1}{\sqrt{2}}(\psi_0 + \psi_1)$ , where  $\psi_0$  and  $\psi_1$  are the first two energy eigen functions of the first two Hermite polynomial.

10. (10%) Using the first order perturbation, calculate the energy of the ground state of an anharmonic oscillator with potential energy function  $V(z) = \frac{kz^2}{2} + cz^4$ , where k, and c are constants.

