『物理化學』部份　總分 50 分

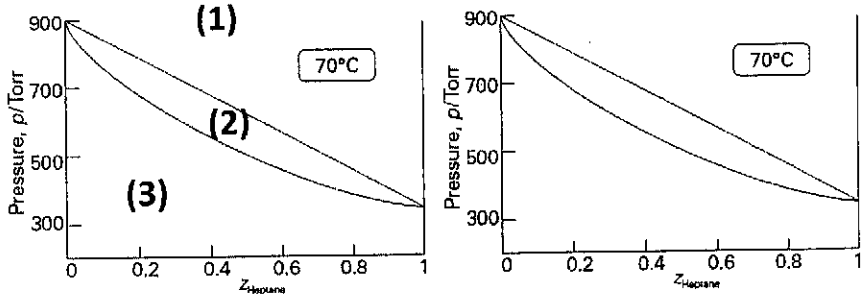
1. Which of the following operators are hermitian? (5%)
   (a) $ix\frac{\partial}{\partial y}$
   (b) $x+i\frac{\partial}{\partial x}$
   (c) $e^{ix}+e^{ix}$
   (d) $x\frac{d}{dx}x$

2. If operators A and B are not coupled, what is their relation of commutator? (5%)
   (a) [A, B]>0
   (b) [A, B]=0
   (c) [A, B]<0

3. Which variable in the the first law of thermodynamics U=q+w is a state function? (5%)
   (a) U
   (b) q
   (c) w

4. One mole of an ideal gas initially at 300 K is expanded from 2.0 L to 10.0 L. What is q and ΔS for this change in state if it is carried out under the following conditions of that The expansion is reversible and adiabatic.. Assume a constant volume heat capacity for the gas, C_V, of 3/2 R. (R=8.314 $JK^{-1}mol^{-1}$) (5%)
   (a) q=0, ΔS>0
   (b) q=0, ΔS=0
   (c) q>0, ΔS>0
   (d) q>0, ΔS=0
   (e) q>0, ΔS<0

5. The figure shown below shows the experimentally determined phase diagrams for the nearly ideal solution of hexane and heptane. Which region is gas phase presented? (5%)



(a) (1)
(b) (2)
(c) (3)
(d) None of above

6. The energy of 1-D particle in a box is $E=\frac{n^2h^2}{8mL^2}$, where n is energy level, m is the mass of the particle, and L the length of the box.
(a) Calculate the separation between the two lowest levels for an O_2 molecule in a one-dimensional container of length 5.0 cm. (5%)
(b) At what value of n does the energy of the molecule reach ½kT at 300 K? (5%)
(The molecular weight of O_2=32, Plank's constant (h) = 6.626x10^{-34} J s, and Boltzmann constant (k) = 1.381x10^{-23} J K^{-1})

7. Calculate the maxima in the radial probability distribution for the 2s orbital. What is the most probable distance from the nucleus for an electron in this orbital (in terms of a_0)? (5%)

(The radial distribution function is $P(r)=\frac{1}{8}\left(\frac{1}{a_0}\right)^3 r^2\left(2-\frac{r}{a_0}\right)^2 e^{-r/a_0}$)

8. Given the reactions (1) and (2) below, determine
(a) $\Delta_rH^\varnothing$ for reaction (3). (5%)
(b) $\Delta_fH^\varnothing$ for HI(g). (5%)
(1) $H_2(g) + I_2(s) \rightarrow 2\ HI(g)$ $\quad \Delta_rH^\varnothing = +52.96$ kJ mol^{-1}
(2) $2\ H_2(g) + O_2(g) \rightarrow 2\ H_2O(g)$ $\quad \Delta_rH^\varnothing = -483.64$ kJ mol^{-1}
(3) $4\ HI(g) + O_2(g) \rightarrow 2\ I_2(s) + 2\ H_2O(g)$

*分析化學*的部份(50%)　　『不可使用計算機』

1. (8%) A Standard Reference Material is certified to contain 94.5 ppm of an organic contaminant in soil. A chemist performs the analysis and gives the value 98.6, 98.4, 97.2, 94.6, and 96.2 ppm. The average and the standard deviations of the measured results are 97.0 and 1.66, respectively. (a) Calculated the 95% confidence interval for the organic contaminant measured by the chemist.(4%) (b) Do the measured results significantly different from the expected results at the 95% confidence level?(2%) (c) At the 95% confidence level, is there any indication of the systematic error in this analysis?(2%)

2. (4%) An atomic absorption method for the determination of Pb^{2+} levels in blood yields an A_{stand} of 0.440 for a standard whose concentration of lead is 2.00 ppb. How many parts per billion of Pb^{2+} occur in a sample of blood if A_{sample} is 0.360?

3. (6%) A 0.5000 M solution of an acid (HA) has a pH of 3.00. Find the K_a and fraction of dissociation, α, for this acid.

4. (6%) The base B has pK_b =5.00. (a) What is the pK_a for acid BH^+?(2%) (b) At what pH is $[BH^+] = [B]$?(2%) (c) What is the quotient $[B]/[BH^+]$ at pH 12.0?(2%)

5. (8%) For the reaction: $Ag(s) + Fe^{3+}(aq) + Cl^-(aq) \rightleftarrows AgCl(s) + Fe^{2+}(aq)$
Write each half-reaction and calculate E^o and K of the reaction.

6. (6%) The following data were obtained by gas-liquid chromatography on a 40-cm packed column:

	t_R, min	W_b, min
Non-retained	1.9	---
A	10.0	0.76
B	10.9	0.86
C	13.4	1.06
D	14.6	1.12

(a) Calculate the selectivity factor (α) of compounds A and B.(3%)
(b) The plate height for the column based on the last peak?(3%)

7. (4%) (a) Describe the difference between reversed-phase and normal-phase chromatography. (2%)
(b) In reversed-phase chromatography, if the eluent becomes less polar, then, the retention time of the compounds will increase or decrease (Explain your answer)?(2%)

8. (4%) A solution of 5.00×10^{-5}M 1,3-dihydroxynaphthelene in 2 M NaOH has a fluorescence intensity of 4.50 at a wavelength of 460 nm. What is the concentration of 1,3-dihydroxynaphthelene with a fluorescence intensity of 3.60 under identical condition?

9. (4%) The accuracy of a spectrophotometer can be evaluated by preparing a solution of 58.80-ppm $K_2Cr_2O_7$ in a 0.0060 M H_2SO_4 and measuring its absorbance at a wavelength of 350 nm using a cell with a pathlength of 1.00 cm. The absorbance should be 0.600. What is the molar absorptivity of $K_2Cr_2O_7$ at the wavelength? (mass of 1 mol $K_2Cr_2O_7$= 294g)

解題用參考資料

$\sqrt{2} = 1.414$, $\sqrt{3} = 1.732$, $\sqrt{5} = 2.236$, $\sqrt{6} = 2.449$, $\sqrt{7} = 2.646$, $\sqrt{8} = 2.828$

Log 2 = 0.301, Log 3 = 0.477, Log 5 = 0.699, Log 7 = 0.845.

Comparing a measured result with a "known" value: $\mu = \bar{x} \pm \frac{ts}{\sqrt{n}}$

Table 1. Values of Student's t for Various Levels of Probability

Degrees of	Confidence Level (%)				
Freedom	80	90	95	99	99.9
1	3.08	6.31	12.7	63.7	637
2	1.89	2.92	4.30	9.92	31.6
3	1.64	2.35	3.18	5.84	12.9
4	1.53	2.13	2.78	4.60	8.60
5	1.48	2.02	2.57	4.03	6.86
6	1.44	1.94	2.45	3.71	5.96
7	1.42	1.90	2.36	3.50	5.40
8	1.40	1.86	2.31	3.36	5.04
9	1.38	1.83	2.26	3.25	4.78
10	1.37	1.81	2.23	3.17	4.59
∞	1.29	1.64	1.96	2.58	3.29

Table 2 Standard Reduction Potentials

Half-reaction at Interface	E^0
$H_2O + e^- \leftrightarrows \frac{1}{2}H_2(g) + 2OH^-$	-0.820 V
$Cr^{3+} + 3e^- \leftrightarrows Cr(s)$	-0.744
$Fe^{2+} + 2e^- \leftrightarrows Fe(s)$	-0.409V
$Cd^{2+} + 2e^- \leftrightarrows Cd(s)$	-0.401 V
$Ni^{2+} + 2e^- \leftrightarrows Ni(s)$	-0.230 V
$CuI(s) + e^- \leftrightarrows Cu(s) + I^-$	-0.185 V
$2H^+ + 2e^- \leftrightarrows H_2(g)$	0.00 V
$Sn^{4+} + 2e^- \leftrightarrows Sn^{2+}$	0.139 V 1MHCl
$AgCl(s) + e^- \leftrightarrows Ag(s) + Cl^-$	+0.223 V
$Hg_2Cl_2(s) + 2e^- \leftrightarrows 2Hg(l) + 2Cl^-$	+0.268 V
$Cu^{2+} + 2e^- \leftrightarrows Cu(s)$	+0.340 V
$Fe^{3+} + e^- \leftrightarrows Fe^{2+}$	+0.771 V
$Ag^+ + e^- \leftrightarrows Ag(s)$	+0.799 V
$Cr_2O_7^{2-} + 14H^+ + 6e^- \leftrightarrows 2\,Cr^{3+} + 7H_2O$	+1.36 V

For the reaction, $aA + ne^- \leftrightarrows bB$,
The Nernst equation and relationship with equilibrium constant K are :

$$E = E^o - \frac{RT}{nF} \ln \frac{A_B^b}{A_A^a}$$

$$E^0 = \frac{0.0592}{n} \log K$$