NATIONAL UNIVERSITY OF SINGAPORE

DEPARTMENT OF CHEMISTRY

ADVANCED PLACEMENT TEST
(SAMPLE)

CM1131   PHYSICAL CHEMISTRY 1

MMM--YYYY ---- Time Allowed: 2 hours

<u>**INSTRUCTIONS TO CANDIDATES**</u>

1.   This paper contains **FOUR (4)** questions and comprises **SIX (6)** printed pages including this cover page.

2.   This is a **CLOSED BOOK** test.

3.   Only non-programmable and non-graphing calculators without remote communication function may be used.

4.   The **Periodic Table** is provided on the last page.

5.   Answer **ALL 4** questions.

6.   Answer each question beginning on a **FRESH** page of the answer booklet.

Question 1

(a) In the morning, a driver inflates the tyres of her car to a recommended pressure of 3.21×10^5 Pa at a temperature of -5 °C. She then drives a few hours to the beach, where the temperature is 28 °C and the volume of tyres increases by 3%. What is the final pressure of the tyres? Does it exceed the manufacturer's recommendation of less than 10% increase in pressure?

(7 marks)

(b) Which isothermal expansion of n = 2 moles of ideal gas would you expect to yield more work?

$P_i = 25$ atm; $V_i = 4.5$ L   to $P_f = 4.5$ atm.

(i) reversible expansion or

(ii) a single step expansion.

(6 marks)

(c) Calculate ΔG at 800 K for the dissociation of Cl_2 (g) to $2Cl$ (g), where P_{Cl_2} = 0.154 Torr and $P_{Cl} = 13.2$ Torr.

Given $\Delta G°_f$ at 298 K: Cl_2 (g) = 0 kJmol^{-1} and Cl (g) = 105.7 kJmol^{-1}; and $\Delta H°_f$ at 298 K: Cl_2 (g) = 0 kJmol^{-1} and Cl (g) = 121.3 kJmol^{-1}. Use K_p rather than K_c for these calculations.

(12 marks)

Question 2

(a) 1 M of the chemical warfare agent phosgene, $COCl_2$, is introduced into a cylinder at 633 K and allowed to decompose to CO and Cl_2, where $K_c = 8.3 \times 10^{-4}$. In order to aid the decomposition process, the volume of the cylinder is changed by 50%, find the concentration of phosgene.

(10 marks)

(b) Calculate the pH when 50 mL of 0.2 M acetic acid is added to 20 mL of 0.5 M NaOH. K_a of acetic acid $= 1.8 \times 10^{-5}$.

(5 marks)

(c) Calculate the pH of 0.1 M citric acid at 25 °C given that $K_{b1} = 1.35 \times 10^{-11}$, $K_{b2} = 5.88 \times 10^{-10}$ and $K_{b3} = 2.5 \times 10^{-8}$.

(5 marks)

(d) For the Zn/Cu voltaic cell, the potential is 1.10 V. Calculate the equilibrium constant for the cell.

(5 marks)

Question 3

(a) $2NH_3 (g) \leftrightarrows N_2 (g) + 3H_2 (g)$ $K = 1.5 \times 10^{-6}$ at 298 K
         $\Delta H°_{f, 298 K} = -11.0$ kcal/mol for $NH_3(g)$

         What is K for the above reaction at 350 K?

(8 marks)

(b)   The experimental data was collected for the hydrolysis of an ester:

Exp't	[Ester]	[H$_2$O]	T (K)	Rate (mol/L·s)	k (L/mol·s)
1	0.100	0.200	288	1.04×10^{-3}	0.0521
2	0.100	0.200	298	2.02×10^{-3}	0.101
3	0.100	0.200	308	3.68×10^{-3}	0.184
4	0.100	0.200	318	6.64×10^{-3}	0.332

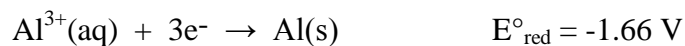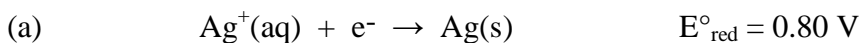   Calculate the collision frequency factor of the reaction.

(7 marks)

(c)   Calculate ΔH for the process where 5.4 moles of liquid water at 18 °C is heated to

         70 °C. The entire process takes place at 1 atm.

(5 marks)

(d)   Describe the apparatus used to measure ΔU and the procedure used.

(5 marks)

Question 4

(a) $Ag^+(aq) + e^- \rightarrow Ag(s)$ $E^\circ_{red} = 0.80$ V

$Al^{3+}(aq) + 3e^- \rightarrow Al(s)$ $E^\circ_{red} = -1.66$ V

An electrochemist requires 2.5 V to light a bulb. She has a silver and aluminium rod and 0.05 M $AgNO_3$ solution. Find the concentration of $Al(NO_3)_3$ she needs to prepare to obtain the required voltage at 298 K.

(8 marks)

(b) Suppose a particular cell reaction is limited by the amount of Au^{3+} present in the cathode electrolyte. If the electrolyte solution has a volume of 300 mL and is 0.35 M in Au^{3+}, how long (in hours) will this cell be able to deliver a current of 30 milliamperes (mA)?

(10 marks)

(c) The sublimed CO_2 gas from 33.0 g of dry ice (CO_2 (s)) is collected in a perfectly elastic balloon at 735 Torr and 21.0 °C. Calculate the work done by the gas in calories, neglecting the volume occupied by the dry ice and assuming ideal gas behavior.

(7 marks)

END OF PAPER

Periodic Table of the Elements

Main groups

1A / 1	2A / 2	3B / 3	4B / 4	5B / 5	6B / 6	7B / 7	8B / 8	8B / 9	8B / 10	1B / 11	2B / 12	3A / 13	4A / 14	5A / 15	6A / 16	7A / 17	8A / 18
1 **H** 1.00794																	2 **He** 4.002602
3 **Li** 6.941	4 **Be** 9.012182											5 **B** 10.811	6 **C** 12.0107	7 **N** 14.0067	8 **O** 15.9994	9 **F** 18.998403	10 **Ne** 20.1797
11 **Na** 22.989770	12 **Mg** 24.3050											13 **Al** 26.981538	14 **Si** 28.0855	15 **P** 30.973761	16 **S** 32.065	17 **Cl** 35.453	18 **Ar** 39.948
19 **K** 39.0983	20 **Ca** 40.078	21 **Sc** 44.955910	22 **Ti** 47.867	23 **V** 50.9415	24 **Cr** 51.9961	25 **Mn** 54.938049	26 **Fe** 55.845	27 **Co** 58.933200	28 **Ni** 58.6934	29 **Cu** 63.546	30 **Zn** 65.39	31 **Ga** 69.723	32 **Ge** 72.64	33 **As** 74.92160	34 **Se** 78.96	35 **Br** 79.904	36 **Kr** 83.80
37 **Rb** 85.4678	38 **Sr** 87.62	39 **Y** 88.90585	40 **Zr** 91.224	41 **Nb** 92.90638	42 **Mo** 95.94	43 **Tc** [98]	44 **Ru** 101.07	45 **Rh** 102.90550	46 **Pd** 106.42	47 **Ag** 107.8682	48 **Cd** 112.411	49 **In** 114.818	50 **Sn** 118.710	51 **Sb** 121.760	52 **Te** 127.60	53 **I** 126.90447	54 **Xe** 131.293
55 **Cs** 132.90545	56 **Ba** 137.327	71 **Lu** 174.967	72 **Hf** 178.49	73 **Ta** 180.9479	74 **W** 183.84	75 **Re** 186.207	76 **Os** 190.23	77 **Ir** 192.217	78 **Pt** 195.078	79 **Au** 196.96655	80 **Hg** 200.59	81 **Tl** 204.3833	82 **Pb** 207.2	83 **Bi** 208.98038	84 **Po** [208.98]	85 **At** [209.99]	86 **Rn** [222.02]
87 **Fr** [223.02]	88 **Ra** [226.03]	103 **Lr** [262.11]	104 **Rf** [261.11]	105 **Db** [262.11]	106 **Sg** [266.12]	107 **Bh** [264.12]	108 **Hs** [269.13]	109 **Mt** [268.14]	110 [271.15]	111 [272.15]	112 [277]		114 [285]		116 [289]		

Transition metals

*Lanthanide series

57 *****La** 138.9055	58 **Ce** 140.116	59 **Pr** 140.90765	60 **Nd** 144.24	61 **Pm** [145]	62 **Sm** 150.36	63 **Eu** 151.964	64 **Gd** 157.25	65 **Tb** 158.92534	66 **Dy** 162.50	67 **Ho** 164.93032	68 **Er** 167.259	69 **Tm** 168.93421	70 **Yb** 173.04

†Actinide series

89 †**Ac** [227.03]	90 **Th** 232.0381	91 **Pa** 231.03588	92 **U** 238.02891	93 **Np** [237.05]	94 **Pu** [244.06]	95 **Am** [243.06]	96 **Cm** [247.07]	97 **Bk** [247.07]	98 **Cf** [251.08]	99 **Es** [252.08]	100 **Fm** [257.10]	101 **Md** [258.10]	102 **No** [259.10]