UNIVERSITY OF TORONTO

FACULTY OF APPLIED SCIENCE AND ENGINEERING

FINAL EXAMINATION - APRIL 2001

First Year - Elective

CHE112H1 - PHYSICAL CHEMISTRY

Examiner - C.E. Chaffey

No aids. A non-programmable calculator may be used.
Answer all <u>seven</u> questions, which have values as indicated; total = *100*.
Many questions require *data* tabulated on page 3.
$R = 8.314472\ \mathrm{J\ K^{-1}\ mol^{-1}}$. $F = 96485\ \mathrm{C\ mol^{-1}}$.
$1\ \mathrm{L} = 10^{-3}\ \mathrm{m^3}$. $T/\mathrm{K} = \theta/°\mathrm{C} + 273.15$. $P° = 1\ \mathrm{bar} = 10^5\ \mathrm{Pa}$.

MARKS

1. Solid ammonium nitrate, NH_4NO_3, is a valuable fertilizer, but it also is explosive. The standard Gibbs free energy of formation is $\Delta G_f°{}_{298} = -184\ \mathrm{kJ\ mol^{-1}}$ for NH_4NO_3. When it explodes, the reaction is

$$NH_4NO_3\ (s) \rightarrow N_2\ (g) + \tfrac{1}{2}\ O_2\ (g) + 2H_2O\ (g).$$

5 **a** By calculating a suitable thermodynamic quantity, show that this explosion reaction tends to occur.

5 **b** Some solid NH_4NO_3 (which occupies negligible volume) explodes completely. The final gas produced has a temperature of 200°C and a volume of 32.0 L when the pressure has decreased to 1.00 bar. What mass of NH_4NO_3 exploded? [Molar mass of NH_4NO_3 = 80.0 g mol^{-1}.]

5 **c** This gas produced expanded irreversibly against a constant external pressure of 1.00 bar. Suppose the work done by the expanding gas was entirely transferred, in the form of kinetic energy, to a fragment of a metal container in which the explosion happened. Find the velocity of the fragment, which has mass 6.00 kg. [Its kinetic energy = ½(mass)(velocity)^2; 1 m s^{-1} = 3.6 km h^{-1}.]

2. Some of the undesirable destruction of ozone, O_3, in the upper atmosphere, may be caused by reaction with nitric oxide, NO, produced from imperfect combustion processes. The destruction reaction $NO + O_3 \rightarrow NO_2 + O_2$ is first order in each reactant. At 298 K, the rate constant is $1.3 \times 10^6\ \mathrm{L\ mol^{-1}\ s^{-1}}$ for the consumption of O_3. At a certain initial time $t = 0$, the concentrations of both NO and O_3 are $7.0 \times 10^{-7}\ \mathrm{mol\ L^{-1}}$.

5 **a** What are the concentrations of [i] NO and [ii] O_3 after 2.00 s?

5 **b** After how long will the concentration of O_3 be 1.0% of its initial value?

3. A maker of electronic parts produces a byproduct solution which initially contains silver ion, Ag^+, at a molar concentration of 0.084 mol L^{-1}. To utilize this solution,
10 500 mL of it is put into one compartment of an electrochemical cell as the electrolyte; the electrode in that compartment is a strip of pure metallic silver, Ag, of initial mass 4.00 g. The other compartment of the cell contains 300 mL of another electrolyte solution initially having pH 4.00; the electrode is a hydrogen electrode, supplied from a rigid tank of volume 0.180 L that initially contains pure gaseous hydrogen, H_2, at a pressure of 2.60 bar. A porous separator between the compartments prevents mixing of the electrolytes but it allows negative ions to pass freely. Everything is at 25°C. Write the cell reaction and find the equilibrium cell voltage E_{cell}.

Data: Standard reduction potentials at 25°C:

$2H^+ + 2e^- \rightarrow H_2$, $E^\circ = 0$; $Ag^+ + e^- \rightarrow Ag$, $E^\circ = +0.7996$ V.

Atomic masses in g mol^{-1}: H 1.008, Ag 107.9.

4. Liquid ethanol, C_2H_5OH, is fed at 25°C to a burner with 1.30 times the stoichiometric amount of air, also at 25°C. Air is 79% N_2 and 21% O_2 by volume. In the burner, complete combustion occurs irreversibly to gaseous products, which leave at 150°C and at 99.0 kPa pressure.

10 **a** What is the mole fraction of N_2 in these gaseous combustion products?

10 **b** Per mole of ethanol, how much heat is given out?

5. A solution is 0.15 mol L^{-1} in ammonia, NH_3, and 0.10 mol L^{-1} in ammonium chloride, NH_4Cl.

5 **a** Calculate the pH of this solution.

10 **b** If 20 mL of a 0.15 mol L^{-1} solution of hydrochloric acid, HCl, is added to 80 mL of the solution of part **a**, by how much will the pH change?

Data: At 25°C, $K_w = 10^{-14}$; for ammonia, NH_3, $K_b = 1.77 \times 10^{-5}$.

6. At what temperature do pure benzene, C_6H_6, and pure ethanol, C_2H_5OH, have
10 equal vapor pressures $P^\bullet$?

7. Nitrosyl bromide, NOBr, can decompose into nitric oxide, NO, and bromine, Br_2, in the gas phase. A reaction vessel of constant volume initially contains pure NOBr. The initial molar volume v of the NOBr is 0.600 m^3 mol^{-1}. Some of the NOBr decomposes, by the reaction $NOBr(g) = NO(g) + \frac{1}{2} Br_2(g)$, and when chemical equilibrium is attained at 50°C the total pressure is 5.90 kPa.

10 **a** Find the equilibrium constant K for this reaction at 50°C.

5 **b** What is the standard molar Gibbs free energy change ΔG_R° for this reaction (or for a reaction with $K = 0.2$)?

5 **c** Why can some products form when the value of ΔG_R° indicates that the reaction is not spontaneous?

Gases and vapours $P^\ominus$ = 1 bar	$c_P{}^\ominus{}_{298}$ J K^{-1} mol^{-1}	$s^\ominus{}_{298}$ J K^{-1} mol^{-1}	$\Delta h_f^\ominus{}_{298}$ kJ mol^{-1}	$\Delta g_f^\ominus{}_{298}$ kJ mol^{-1}	$c_P{}^\ominus{}_{600}$ J K^{-1} mol^{-1}	T_{bp} K	a, Pa m^6 mol^{-2}	$10^6 b$ m^3 mol^{-1}	Henry's K_{298}, H_2O
Hydrogen, H_2	28.84	130.68	0	0	29.33	20.3	0.0245	26.5	7.11 GPa
Nitrogen, N_2	29.12	191.61	0	0	30.11	77.4	0.137	38.7	8.54 GPa
Oxygen, O_2	29.38	205.15	0	0	32.09	90.2	0.138	31.9	4.27 GPa
Ozone, O_3	39.24	238.93	142.67	163.18	49.86	161.8	0.357	48.7	505 MPa
Water, H_2O (g)	33.59	188.83	-241.83	-228.58	36.33	373.2	0.554	30.5	
Carbon monoxide, CO	29.14	197.65	-110.53	-137.17	30.44	81.6	0.147	39.5	5.61 GPa
Carbon dioxide, CO_2	37.13	213.80	-393.52	-394.39	47.32	194.8_{subl}	0.366	42.9	159 MPa
Methane, CH_4	37.13	186.25	-74.87	-50.77	52.23	111.8	0.230	43.1	4.27 GPa
Acetylene, C_2H_2	44.10	200.96	226.73	209.20	58.29	188.4_{subl}	0.452	52.2	135 MPa
Ethylene, C_2H_4	42.89	219.33	52.47	68.42	70.66	169.5	0.461	58.2	1.18 GPa
Ethane, C_2H_6	52.63	229.60	-84.68	-32.83	89.33	184.5	0.558	65.1	2.76 GPa
Formaldehyde, HCHO	35.40	218.95	-115.90	-109.92	48.22	249.6	0.718	63.5	reacts
Formic acid, HCOOH (g)	45.23	248.85	-378.61	-350.97	67.03	373.9	1.78	110.	1.01 kPa
Methanol, CH_3OH (g)	43.89	239.81	-201.17	-162.45	67.03	337.8	0.958	66.6	25.2 kPa
Ketene, $CH_2C{=}O$	51.76	241.90	-61.09	-60.24	70.67	232.0	0.648	60.8	reacts
Ethylene oxide, C_2H_4O	47.90	243.01	-52.64	-13.16	86.31	283.8	0.892	67.8	reacts
Acetaldehyde, CH_3CHO	54.64	264.33	-166.36	-133.24	85.86	293.8	1.11	86.0	427 kPa
Acetic acid, CH_3COOH (g)	66.53	282.61	-434.84	-376.59	105.23	391.3	1.78	107.	1.01 kPa
Ethanol, C_2H_5OH (g)	65.44	282.70	-234.81	-168.20	107.49	351.4	1.22	84.3	29.2 kPa
Dimethyl ether, $(CH_3)_2O$	65.81	267.17	-184.05	-112.82	105.27	249.2	0.876	78.0	5.61 MPa
Ethylene glycol, HOC_2H_4OH (g)	97.07	323.66	-389.32	-304.35	136.90	470.5	2.74	123.	1.39 Pa

Liquids $P^\ominus$ = 1 bar	ρ_{298} kg m^{-3}	$c_P{}^\ominus{}_{298}$ J K^{-1} mol^{-1}	$s^\ominus{}_{298}$ J K^{-1} mol^{-1}	$\Delta h_f^\ominus{}_{298}$ kJ mol^{-1}	$\Delta g_f^\ominus{}_{298}$ kJ mol^{-1}	$c_P{}^\ominus{}_{298}$(g) J K^{-1} mol^{-1}	T_{mp} K	$\Delta h_{fus,mp}$ kJ mol^{-1}	K_f, K kg mol^{-1}	$P^\bullet{}_{298}$ kPa	T_{bp} K	$\Delta h_{vap,bp}$ kJ mol^{-1}	K_b, K kg mol^{-1}	Henry's K_{298}, H_2O
Water, H_2O	997.0	75.3	69.95	-285.83	-237.14	33.59	273.2	6.01	1.86	3.17	373.2	40.65	0.513	
n-Pentane, C_5H_{12}	621.2	167.2	263.94	-172.75	-9.11	120.21	143.5	8.40	1.47	68.67	309.2	25.79	2.22	6.85 GPa
Cyclohexane, C_6H_{12}	773.9	154.9	205.32	-155.82	27.01	106.27	279.7	2.68	20.4	13.60	353.9	29.97	2.92	991 MPa
n-Heptane, C_7H_{16}	679.3	224.7	329.58	-223.86	1.55	165.98	182.6	14.03	1.98	6.59	371.7	31.77	3.62	12.6 GPa
Isooctane, C_8H_{18}	687.7	239.1	329.47	-258.66	7.47	188.87	165.8	9.20	2.84	7.16	372.4	30.79	4.28	17.9 GPa
Benzene, C_6H_6	871.1	136.0	173.13	49.21	124.75	81.67	278.6	9.87	5.11	13.11	353.2	30.72	2.64	30.8 MPa
Toluene, C_7H_8	861.6	157.3	220.77	12.22	114.23	103.64	178.2	6.64	3.67	4.03	383.8	33.18	3.40	37.0 MPa
Methanol, CH_3OH	786.7	81.1	130.92	-237.85	-166.67	43.89	175.6	3.22	2.56	18.24	337.8	35.21	0.863	25.2 kPa
Ethanol, C_2H_5OH	784.9	112.3	165.27	-275.86	-174.25	65.44	159.0	4.93	1.96	8.72	351.4	38.56	1.23	29.2 kPa

Solids $P^\ominus$ = 1 bar	ρ_{298} kg m^{-3}	$c_P{}^\ominus{}_{298}$ J K^{-1} mol^{-1}	$s^\ominus{}_{298}$ J K^{-1} mol^{-1}	$\Delta h_f^\ominus{}_{298}$ kJ mol^{-1}	$\Delta g_f^\ominus{}_{298}$ kJ mol^{-1}	$c_P{}^\ominus{}_{600}$ J K^{-1} mol^{-1}	T_{mp} K	$\Delta h_{fus,mp}$ kJ mol^{-1}
Graphite, C (gr)	2250	8.51	5.74	0	0	16.88	3915_{subl}	706.7_{subl}
Diamond, C (dia)	3513	6.13	2.37	1.90	2.90	16.12		
Calcium, Ca	1540	25.31	41.42	0	0	29.55	1115	8.54
– carbide, CaC_2	2220	62.72	69.96	-59.80	-64.89	73.31		
– carbonate, $CaCO_3$	2710	83.47	92.90	-1206.92	-1128.81	109.87	1603	36
– hydride, CaH_2	1700	41.00	41.40	-176.98	-138.01	52.21	1273	22
– oxide, CaO	3340	42.12	38.07	-635.09	-603.51	50.48	3172	80
– hydroxide, $Ca(OH)_2$	2200	87.49	83.39	-986.09	-898.47	107.44	1023	29