CHEMISTRY 108 **Final** Name _____
SECTION 01 8:00 am - 9:50 am Tuesday, May 12, 1998

Please read thoroughly and answer all questions. Points available are in parentheses.

(1.) Please consider the following balanced reaction, and columns of experimental data, which were measured at 700 K:

$$CH_3CHO\ (g) \quad ----- > \quad CO\ (g) \quad + \quad CH_4\ (g)$$

$[CH_3CHO]_t$ (mol L^{-1})	t (s)	rate of reaction CH_3CHO (mol L^{-1} s^{-1})
0.200	0	
0.153	20	
0.124	40	
0.104	60	
0.090	80	
0.079	100	

(a) Is the reaction homogeneous? Please determine the overall order of the reaction. (*10*)
(b) Please write the rate law expression for the reaction, and fill in the column above headed "rate of CH_3CHO reaction." (*5*)
(c) Please write the overall reaction as elementary steps, and encircle any intermediates. Please propose which would be the rate-determining step. (*5*)

(2.) Please consider the following balanced reaction, at 673 K:

$$HCOOH\ (g) \qquad CO\ (g) + H_2O\ (g) \qquad K_p = 1.60 \times 10^{10}$$

(a) Please calculate K_c (*5*) (R = 0.0821 L atm/mol/K)
(b) Using whatever is necessary from the data below, please indicate if the reaction to produce HCOOH is exothermic or endothermic at 673 K (*5*)

	ΔH_f^0 (kJ/mol)	S^0 (J/mol/K)	ΔG_f^0 (kJ/mol)
CO (g)	- 110	197.9	- 137.3
H_2O (g)	- 241.8	188.7	- 228.6
HCOOH (g)	- 363	251	+ 335

(c) What is ΔG^0 at 673 K? Is the (l ----> r) reaction spontaneous at 673 K? (*5*)
(d) If the reaction changes from spontaneous to non-spontaneous at a particular temperature, please determine that temperature. (*5*)

(e) A vessel of volume 100.0 mL is charged with 2.80 g of CO, 1.80 g H_2O, and 4.60 x 10^{-7}g of HCOOH, then sealed, and brought to 673 K. Please determine the reaction quotient, *Q*, under the initial conditions, and then indicate in which direction the reaction will proceed to attain equilibrium. Please answer one of (l ----> r), (r ----> l), or no shift. (*5*)

(f) Suppose you had also added in 10.00 g of the inert gas, helium (He), initially. Would this have made a difference to *Q*? Please explain your answer. (*5*)

(g) Suppose now that the system attains equilibrium at 673 K, and that you then introduce a further 1.00 g H_2O. Will the system be disturbed from equilibrium? If so, which way will the equilibrium shift? Please answer one of (l ----> r), (r ----> l), or no shift. (*5*)

(h) Which direction will the equilibrium shift if the system is cooled to 598 K? Please answer one of (l ----> r), (r ----> l), or no shift (*5*)

(i) Now, you perform the same reaction as in (e), but you use a vessel of volume 195.0 mL. What effect will this have on the position of the equilibrium relative to that in (e)? Please answer one of (l ----> r), (r ----> l), or no shift (*5*)

(3.) You have a solution of 100.0 mL 0.020 M Ag^+ (aq), (with innocent counter-ion) and another solution of 100.0 mL 0.100 M sulfurous acid (H_2SO_3) solution? (K_{a1} = 1.2 x 10^{-2}, K_{a2} = 6.6 x 10^{-8})

(i) Please write the equations for which K_{a1} and K_{a2} above are equilibrium constants (*5*)

(ii) What pH is required to precipitate Ag_2SO_3 (s)? (K_{sp} = 1.5 x 10^{-14}) (*10*)

(iii) You set the pH = 2.00 without changing the volume of solution significantly. What is the $[SO_3^{2-}]$ now? Will Ag_2SO_3 (s) form now? How did you set the pH = 2.00 without changing the volume significantly? (*5*)

(4.) You have Pt (s) and Au (s) electrodes, and you are going to use these to prepare a galvanic cell with Pt^{2+} (aq) and Au^{3+} (aq) electrolytes.

(i) Please write the anode and cathode reactions (*6*)

(ii) Please write the overall cell reaction, with the overall cell potential (*4*)

(iii) Please write the short-hand notation for the galvanic cell (*5*)

(iv) Please assume that you have two galvanic cells; one is under standard conditions, and the other has the following electrolyte concentrations: $[Pt^{2+}$ (aq)] = 0.001 M and $[Au^{3+}$ (aq)] = 1.000 M. Which of the two cells is closer to equilibrium, and why? (*5*)

(5.) (a) Please write the formulae for the following: (*12*)

(i) butanal (ii) 2-butanone (iii) 2,2-dimethylpropane (iv) 2-butene

(b) Please describe through use of abbreviated general formulae, the following functional groups: (*8*)

(i) alcohol (ii) ether (iii) amine (iv) ester

(6.) (a) Please calculate the molar solubility of iron (III) phosphate, $FePO_4$, in pure water (K_{sp} = 4.0 x 10^{-27}). (*5*)

(b) The solubility of $FePO_4$ increases drastically when oxalate ion (ox) is introduced, owing to the formation of the complex $[Fe(ox)_3]^{3-}$ (K_{form} = 3.3 x 10^{20}). Please write the equilibria together, and determine K_c for the overall equation.(*5*)

(c) Please determine the molar solubility of $FePO_4$ in 0.1 M sodium oxalate solution. (*5*)

(d) What is the charge on the oxalate ion? Please draw the enantiomers of $[Fe(ox)_3]^{3-}$ (*5*)

(e) Please assign the *d*-orbital splitting diagram for $[Fe(ox)_3]^{3-}$, given that the complex is low-spin. Is the complex diamagnetic or paramagnetic? (*5*)

(f) Please give the name for $Na_3[Fe(ox)_3]$. (*5*)

(7.) Please write the following as nuclear reactions, and please fully report the atomic masses and atomic numbers of all the expected reaction constituents:

(i) ^{100}Sn decays by positron emission (*5*)

(ii) ^{110}Rh decays by β-emission (*5*)

(iii) ^{234}U decays by α-emission (*5*)

(iv) The isotope ^{197}Au has actual mass 196.966 u. Please calculate the nuclear binding energy per nucleus and per nucleon in units of MeV (1eV = 1.602 x 10^{-19} J) (*5*)

1p = 1.00727252 u
1n = 1.008665 u
c = 3.00 x 10^8 m/s
1u = 1.6606 x 10^{-24} g

(8.) Please calculate the pH of the solutions below. Please use **Table 1**, below, to determine the relevant K_a and K_b values. (*5* x *5*)

(a) A 0.030 M solution of formic acid

(b) A 0.080 M solution of sodium nitrite

(c) A buffer which is 0.300 M in formic acid and 0.100 M in sodium formate

(d) A 0.200 M solution of ammonium nitrate

(e) A solution which is 1.100 M in pyridinium nitrate, 0.100 M in sodium nitrate, and 0.250 M in nitric acid

Table 1:

Name of acid	Formula	K_a
Phenol	C_6H_5OH	1.3 x 10^{-10}
Nitrous Acid	HNO_2	7.1 x 10^{-4}
Formic Acid	HCOOH	1.8 x 10^{-4}

Name of Base	Formula	K_b
Pyridine	C_5H_5N	1.5 x 10^{-9}
Ammonia	NH_3	1.8 x 10^{-5}