Spring 1996 — Saturday, June 22, 1996

Time: 2 hours — **Prof. Ayssar Nahlé**

Chemistry 215

Analytical Chemistry

Final

Name: ....
Family First name

I.D. number: ...._ ....

Grade

I	/ 18
II	/ 16
III	/ 16
IV	/ 20
V	/ 15
VI	/ 15
total	/100

Good luck

I. A 2.00×10^{-3} M NH_4NO_3 solution is subjected to a bacterial action which results in the reduction of NO_3^- to NH_4^+. The reduction is monitored potentiometrically with ammonium- and nitrate-selective electrodes. The potential of the ammonium- selective electrode was +0.0401 V before the bacterial action and + 0.0490 V afterwards, whereas the initial potential of the nitrate-selective electrode was +0.0886 V. Calculate the potential of the nitrate electrode after the bacterial action (assume activity equals concentration).

Potential of the nitrate electrode after the bacterial action = ... V

II. The H^+ ion concentration in a CH_3COOH-CH_3COONa buffer is 7.83×10^{-6} M. Calculate the molarities of CH_3COOH and CH_3COONa, given that $[H^+]$ becomes 1.2×10^{-5} M when 41.6 millimoles of HCl is added to one liter of buffer.

$[CH_3COOH]$ = ... M

$[CH_3COONa]$ = ... M

III. The transmittance of solution **X** which contains M^{3+} and M^{2+} ions was 0.182 in a 1.00 cm cell at 431 nm, where only M^{3+} ions absorb with ε_{431} = 450 $L mol^{-1} cm^{-1}$. The potential of a platinum indicator electrode immersed in solution **X**, which depends on the ratio $[M^{3+}]/[M^{2+}]$, was +0.0558 V versus the saturated calomel electrode. Calculate the concentrations of M^{3+} and M^{2+} ions in solution **X**, given that E^0 (for M^{3+}, M^{2+}) = +0.402 V.

$[M^{3+}]$ = ... <u>**M**</u>

$[M^{2+}]$ = ... <u>**M**</u>

IV. **a)** Construct the potentiometric titration curve (versus SHE) for the titration of 50.00 mL of 0.0500N Fe(II) solution with 0.1000 N Ce(IV) solution (**both solutions are 1.0 M in H_2SO_4**). (Calculate the potential of platinum electrode immersed in the Fe^{2+} solution after each addition of Ce^{4+} as indicated in the table below; and fill in the table the calculated potentials vs. SHE).

b) Calculate the first derivative ($\Delta E/\Delta V$) and the second derivative ($\Delta^2E/\Delta V^2$) and the corresponding volumes V' and V" respectively (insert the results in the table).

c) On the provided graph paper, plot the first derivative ($\Delta E/\Delta V$) versus V'.

$V_{Ce(IV)}$, mL	E, V	$\Delta E/\Delta V$	V'	$\Delta^2E/\Delta V^2$	V"
5.00					
10.00					
12.50					
20.00					
24.00					
24.95					
25.00					
25.05					
25.50					
30.00					
50.00					

V. **A)** Solid $AgNO_3$ is added to a solution which is 0.0020 M in CrO_4^{2-} and 0.090 M in Cl^-. **a)** Which precipitate will be precipitated first? **b)** What percentage of Cl^- has been precipitated when Ag_2CrO_4 starts to precipitate?

.... **will be precipitated first**

% Cl^- = ...

B) Calculate the absolute and the relative standard deviations [S_y and $\frac{S_y}{y}$] for the following expression, and round the result to the appropriate significant figures:

$$y = \frac{[15.321(\pm 0.003) - 7.12(\pm 0.04)] \times \sqrt{6.376(\pm 0.005)}}{[\log 58.3(\pm 0.2)]^2} = 6.6423629....(\pm..???)$$

$\frac{S_y}{y}$ = ...

S_y = ...

y = ... ± ....

VI. Solution **A** of phosphates consumed 11.22 mL of standard acid solution when titrated in the presence of phenolphthalein and an additional 33.66 mL for the subsequent titration to methyl orange end point. Calculate the pH of solution **A**.

pH = ...

Dissociation constants for acids.

Acid	Equilibrium equation	K_a	pK_a
Acetic	$CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$	1.8×10^{-5}	4.74
Aluminum hydroxide	$Al(OH)_3 \rightleftharpoons H^+ + AlO_2^- + H_2O$	4×10^{-13}	12.4
Aluminum ion	$[Al(H_2O)_6]^{3+} \rightleftharpoons H^+ + [Al(H_2O)_5(OH)]^{2+}$	1.1×10^{-5}	4.96
Ammonium ion	$NH_4^+ \rightleftharpoons H^+ + NH_3$	5.6×10^{-10}	9.25
Antimony(III) hydroxide	$Sb(OH)_3 \rightleftharpoons H^+ + SbO_2^- + H_2O$	1×10^{-11}	11.0
Arsenic	$H_3AsO_4 \rightleftharpoons H^+ + H_2AsO_4^-$	6.0×10^{-3} (K_{a_1})	2.22
	$H_2AsO_4^- \rightleftharpoons H^+ + HAsO_4^{2-}$	1×10^{-7} (K_{a_2})	7.0
	$HAsO_4^{2-} \rightleftharpoons H^+ + AsO_4^{3-}$	3×10^{-12} (K_{a_3})	11.5
Benzoic	$C_6H_5COOH \rightleftharpoons H^+ + C_6H_5COO^-$	6.6×10^{-5}	4.18
Boric	$H_3BO_3 \rightleftharpoons H^+ + H_2BO_3^-$	6.0×10^{-10}	9.22
Carbonic	$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$	4.2×10^{-7} (K_{a_1})	6.38
	$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$	4.8×10^{-11} (K_{a_2})	10.32
Chloroacetic	$ClCH_2COOH \rightleftharpoons H^+ + ClCH_2COO^-$	1.4×10^{-3}	2.85
Chromic	$H_2CrO_4 \rightleftharpoons H^+ + HCrO_4^-$	$\simeq 10^{-1}$ (K_{a_1})	1.0
	$HCrO_4^- \rightleftharpoons H^+ + CrO_4^{2-}$	3.2×10^{-7} (K_{a_2})	6.49
Copper(II) hydroxide	$Cu(OH)_2 \rightleftharpoons H^+ + HCuO_2^-$	1.5×10^{-16} (K_{a_1})	15.82
	$HCuO_2^- \rightleftharpoons H^+ + CuO_2^{2-}$	8×10^{-14} (K_{a_2})	13.1
Dichloroacetic	$Cl_2CHCOOH \rightleftharpoons H^+ + Cl_2CHCOO^-$	5.5×10^{-2}	1.26
Formic	$HCOOH \rightleftharpoons H^+ + HCOO^-$	2.1×10^{-4}	3.68
Hydrocyanic	$HCN \rightleftharpoons H^+ + CN^-$	4×10^{-10}	9.4
Hydrofluoric	$HF \rightleftharpoons H^+ + F^-$	6.9×10^{-4}	3.16
Hydrogen peroxide	$H_2O_2 \rightleftharpoons H^+ + HO_2^-$	2.4×10^{-12}	11.62
Hydrogen sulfide	$H_2S \rightleftharpoons H^+ + HS^-$	1.0×10^{-7}(K_{a_1})	7.00
	$HS \rightleftharpoons H^+ + S^{2-}$	1.0×10^{-14}(K_{a_2})	14.00
Hypochlorous	$HClO \rightleftharpoons H^+ + ClO^-$	3.2×10^{-8}	7.49
Iron(III) ion	$[Fe(H_2O)_6]^{3+} \rightleftharpoons H^+ + [Fe(H_2O)_5(OH)]^{2+}$	8.9×10^{-4}	3.05
Lead(II) hydroxide	$Pb(OH)_2 \rightleftharpoons H^+ + HPbO_2^-$	2×10^{-16}	15.7
Nitrous	$HNO_2 \rightleftharpoons H^+ + NO_2^-$	4.5×10^{-4}	3.35
Oxalic	$H_2C_2O_4 \rightleftharpoons H^+ + HC_2O_4^-$	3.8×10^{-2}(K_{a_1})	1.42
	$HC_2O_4^- \rightleftharpoons H^+ + C_2O_4^{2-}$	5.0×10^{-5}(K_{a_2})	4.30
Periodic	$HIO_4 \rightleftharpoons H^+ + IO_4^-$	2.3×10^{-2}	1.64
Phenol	$C_6H_5OH \rightleftharpoons H^+ + C_6H_5O^-$	1×10^{-10}	10.0
Phosphoric	$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^-$	7.5×10^{-3}(K_{a_1})	2.12
	$H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{2-}$	6.2×10^{-8}(K_{a_2})	7.21
	$HPO_4^{2-} \rightleftharpoons H^+ + PO_4^{3-}$	1×10^{-12}(K_{a_3})	12.0
Phosphorous	$H_3PO_3 \rightleftharpoons H^+ + H_2PO_3^-$	1.6×10^{-2}(K_{a_1})	1.80
	$H_2PO_3^- \rightleftharpoons H^+ + HPO_3^{2-}$	7×10^{-7}(K_{a_2})	6.2
Silicic (meta)	$H_2SiO_3 \rightleftharpoons H^+ + HSiO_3^-$	3.2×10^{-10}(K_{a_1})	9.49
	$HSiO_3^- \rightleftharpoons H^+ + SiO_3^{2-}$	6.3×10^{-12}(K_{a_2})	11.80
Sulfamic	$HNH_2SO_3 \rightleftharpoons H^+ + NH_2SO_3^-$	1.1×10^{-1}	0.96
Sulfuric	$H_2SO_4 \rightleftharpoons H^+ + HSO_4^-$	1.0×10^{2}(K_{a_1})	−2.00
	$HSO_4^- \rightleftharpoons H^+ + SO_4^{2-}$	1.2×10^{-2}(K_{a_2})	1.92
Sulfurous	$H_2SO_3 \rightleftharpoons H^+ + HSO_3^-$	1.72×10^{-2}(K_{a_1})	
	$HSO_3^- \rightleftharpoons H^+ + SO_3^{2-}$	6.43×10^{-8}(K_{a_2})	
Tartaric	$H_2C_4H_4O_6 \rightleftharpoons H^+ + HC_4H_4O_6^-$	1.1×10^{-3}(K_{a_1})	2.96
	$HC_4H_4O_6^- \rightleftharpoons H^+ + C_4H_4O_6^{2-}$	6.9×10^{-5}(K_{a_2})	4.16
Thiocyanic	$HSCN \rightleftharpoons H^+ + SCN^-$	1.4×10^{-1}	0.85
Thiosulfuric	$H_2S_2O_3 \rightleftharpoons H^+ + HS_2O_3^-$	2.0×10^{-2}(K_{a_1})	1.70
	$HS_2O_3^- \rightleftharpoons H^+ + S_2O_3^{2-}$	3.2×10^{-3}(K_{a_2})	2.49
Tin(II) hydroxide	$Sn(OH)_2 \rightleftharpoons H^+ + HSnO_2^-$	4×10^{-15}	14.4
Trichloroacetic	$Cl_3CCOOH \rightleftharpoons H^+ + Cl_3CCOO^-$	1.3×10^{-1}	0.89
Zinc hydroxide	$Zn(OH)_2 \rightleftharpoons H^+ + HZnO_2^-$	1×10^{-17}(K_{a_1})	17.0
	$HZnO_2^- \rightleftharpoons H^+ + ZnO_2^{2-}$	2×10^{-13}(K_{a_2})	12.7
Zinc ion	$[Zn(H_2O)_4]^{2+} \rightleftharpoons H^+ + [Zn(H_2O)_3(OH)]^+$	2.5×10^{-10}	9.60

Table A.3. *Solubility product constants*

Substance	Equilibrium equation	K_{sp}	pK_{sp}
Carbonates (continued)			
Magnesium carbonate	$MgCO_3 \rightleftharpoons Mg^{2+} + CO_3^{2-}$	4×10^{-5}	4.4
Manganese(II) carbonate	$MnCO_3 \rightleftharpoons Mn^{2+} + CO_3^{2-}$	9×10^{-11}	10.1
Mercury(I) carbonate	$Hg_2CO_3 \rightleftharpoons Hg_2^{2+} + CO_3^{2-}$	9×10^{-17}	16.1
Nickel carbonate	$NiCO_3 \rightleftharpoons Ni^{2+} + CO_3^{2-}$	7×10^{-9}	8.2
Silver carbonate	$Ag_2CO_3 \rightleftharpoons 2Ag^+ + CO_3^{2-}$	8.2×10^{-12}	11.09
Strontium carbonate	$SrCO_3 \rightleftharpoons Sr^{2+} + CO_3^{2-}$	7×10^{-10}	9.2
Zinc carbonate	$ZnCO_3 \rightleftharpoons Zn^{2+} + CO_3^{2-}$	2×10^{-11}	10.7
Chlorides			
Copper(I) chloride	$CuCl \rightleftharpoons Cu^+ + Cl^-$	3.2×10^{-7}	6.49
Lead chloride	$PbCl_2 \rightleftharpoons Pb^{2+} + 2Cl^-$	1.6×10^{-5}	4.80
Mercury(I) chloride	$Hg_2Cl_2 \rightleftharpoons Hg_2^{2+} + 2Cl^-$	1.1×10^{-18}	17.96
Silver chloride	$AgCl \rightleftharpoons Ag^+ + Cl^-$	1.8×10^{-10}	9.74
Thallium(I) chloride	$TlCl \rightleftharpoons Tl^+ + Cl^-$	3.5×10^{-4}	3.46
Chromates			
Barium chromate	$BaCrO_4 \rightleftharpoons Ba^{2+} + CrO_4^{2-}$	1.2×10^{-10}	9.92
Calcium chromate	$CaCrO_4 \rightleftharpoons Ca^{2+} + CrO_4^{2-}$	7.1×10^{-4}	3.15
Copper(II) chromate	$CuCrO_4 \rightleftharpoons Cu^{2+} + CrO_4^{2-}$	3.6×10^{-6}	5.44
Lead chromate	$PbCrO_4 \rightleftharpoons Pb^{2+} + CrO_4^{2-}$	2×10^{-14}	13.7
Mercury(I) chromate	$Hg_2CrO_4 \rightleftharpoons Hg_2^{2+} + CrO_4^{2-}$	2×10^{-9}	8.7
Silver chromate	$Ag_2CrO_4 \rightleftharpoons 2Ag^+ + CrO_4^{2-}$	1.9×10^{-12}	11.72
Strontium chromate	$SrCrO_4 \rightleftharpoons Sr^{2+} + CrO_4^{2-}$	3.6×10^{-5}	4.44
Cyanides			
Mercury(I) cyanide	$Hg_2(CN)_2 \rightleftharpoons Hg_2^{2+} + 2CN^-$	5×10^{-40}	39.3
Silver cyanide	$AgCN \rightleftharpoons Ag^+ + CN^-$	1.6×10^{-14}	13.80
Ferrocyanides			
Copper(II) ferrocyanide	$Cu_2[Fe(CN)_6] \rightleftharpoons 2Cu^{2+} + [Fe(CN)_6]^{4-}$	1.3×10^{-16}	15.89
Silver ferrocyanide	$Ag_4[Fe(CN)_6] \rightleftharpoons 4Ag^+ [Fe(CN)_6]^{4-}$	1.6×10^{-41}	40.80
Zinc potassium ferrocyanide	$K_2Zn_3[Fe(CN)_6]_2 \rightleftharpoons 2K^+ + 3Zn^{2+} + 2[Fe(CN)_6]^{4-}$	1×10^{-95}	95.0
Fluorides			
Barium fluoride	$BaF_2 \rightleftharpoons Ba^{2+} + 2F^-$	2.4×10^{-5}	4.62
Calcium fluoride	$CaF_2 \rightleftharpoons Ca^{2+} + 2F^-$	1.7×10^{-10}	9.77
Lead fluoride	$PbF_2 \rightleftharpoons Pb^{2+} + 2F^-$	2.7×10^{-8}	7.57
Magnesium fluoride	$MgF_2 \rightleftharpoons Mg^{2+} + 2F^-$	6.5×10^{-9}	8.19
Strontium fluoride	$SrF_2 \rightleftharpoons Sr^{2+} + 2F^-$	7.9×10^{-10}	9.10

Critical Values for Rejection Quotient Q

Number of Observations	Q_{crit} 90% Confidence	96% Confidence	99% Confidence
3	0.94	0.98	0.99
4	0.76	0.85	0.93
5	0.64	0.73	0.82
6	0.56	0.64	0.74
7	0.51	0.59	0.68
8	0.47	0.54	0.63
9	0.44	0.51	0.60
10	0.41	0.48	0.57

Standard and formal potentials, E^0 and $E^{0\prime}$, at 25° C

Half reaction	E^0, volts	$E^{0\prime}$, volts	Conditions for the formal potentials
1. Acidic solutions			
$2ICl_2^- + 2e \rightleftharpoons I_2 + 4Cl^-$	+1.06		
$HNO_2 + H^+ + e \rightleftharpoons NO + H_2O$	+1.00		
$NO_3^- + 4H^+ + 3e \rightleftharpoons NO + 2H_2O$	+0.96		
$NO_3^- + 3H^+ + 2e \rightleftharpoons HNO_2 + H_2O$	+0.94		
$NO_3^- + 10H^+ + 8e \rightleftharpoons NH_4^+ + 3H_2O$	+0.87		
$2Hg^{2+} + 2e \rightleftharpoons Hg_2^{2+}$	+0.920		
$Cu^{2+} + I^- + e \rightleftharpoons CuI$	+0.86		
$Ag^+ + e \rightleftharpoons Ag$	+0.7994		
$Hg_2^{2+} + 2e \rightleftharpoons 2Hg$	+0.789		
$Fe^{3+} + e \rightleftharpoons Fe^{2+}$	+0.771		
		+0.732	1 M $HClO_4$
		+0.700	1 M HCl
		+0.674	1 M H_2SO_4
		+0.46	2 M H_3PO_4
$O_2 + 2H^+ + 2e \rightleftharpoons H_2O_2$	+0.682		
$I_2(aq) + 2e \rightleftharpoons 2I^-$	+0.6197[b]		
$MnO_4^- + e \rightleftharpoons MnO_4^{2-}$	+0.564		
$H_3AsO_4 + 2H^+ + 2e \rightleftharpoons H_3AsO_3 + H_2O$	+0.559		
		+0.577	1 M HCl, 1 M $HClO_4$
$[I_3]^- + 2e \rightleftharpoons 3I^-$	+0.536		
$I_2 + 2e \rightleftharpoons 2I^-$	+0.5355[b]		
$Cu^+ + e \rightleftharpoons Cu$	+0.521		
$H_2SO_3 + 4H^+ + 4e \rightleftharpoons S + 3H_2O$	+0.45		
$Ag_2CrO_4 + 2e \rightleftharpoons 2Ag + CrO_4^{2-}$	+0.446		
$2H_2SO_3 + 2H^+ + 4e \rightleftharpoons S_2O_3^{2-} + 3H_2O$	+0.40		
$[Fe(CN)_6]^{3-} + e \rightleftharpoons [Fe(CN)_6]^{4-}$	+0.356		
		+0.71	1 M HCl
$Cu^{2+} + 2e \rightleftharpoons Cu$	+0.337		
$Hg_2Cl_2 + 2e \rightleftharpoons 2Hg + 2Cl^-$	+0.2680		
		+0.3337	0.1 M KCl
		+0.2801	1 M KCl
		+0.2412	KCl satur.
$AgCl + e \rightleftharpoons Ag + Cl^-$	+0.2224		
$SO_4^{2-} + 4H^+ + 2e \rightleftharpoons H_2SO_3 + H_2O$	+0.17		
$Cu^{2+} + e \rightleftharpoons Cu^+$	+0.153		
$Sn^{4+} + 2e \rightleftharpoons Sn^{2+}$	+0.15		
$[SnCl_6]^{2-} + 2e \rightleftharpoons [SnCl_4]^{2-} + 2Cl^-$		+0.14	1 M HCl
$S + 2H^+ + 2e \rightleftharpoons H_2S$	+0.141		
$AgBr + e \rightleftharpoons Ag + Br^-$	+0.095		
$S_4O_6^{2-} + 2e \rightleftharpoons 2S_2O_3^{2-}$	+0.08		
$[Ag(S_2O_3)_2]^{3-} + e \rightleftharpoons Ag + 2S_2O_3^{2-}$	+0.01		
$2H^+ + 2e \rightleftharpoons H_2$	0.000		

Standard and formal potentials, E^0 and $E^{0'}$, at 25° C

Half reaction	E^0, volts	$E^{0'}$, volts	Conditions for the formal potentials
1. Acidic solutions			
$F_2 + 2H^+ + 2e \rightleftharpoons 2HF$	+3.06		
$F_2 + 2e \rightleftharpoons 2F^-$	+2.85		
$S_2O_8^{2-} + 2e \rightleftharpoons 2SO_4^{2-}$	+2.01		
$Co^{3+} + e \rightleftharpoons Co^{2+}$	+1.82		
$H_2O_2 + 2H^+ + 2e \rightleftharpoons 2H_2O$	+1.77		
$MnO_4^- + 4H^+ + 3e \rightleftharpoons MnO_2 + 2H_2O$	+1.695		
$Ce^{4+} + e \rightleftharpoons Ce^{3+}$		+1.70	1 M $HClO_4$
		+1.61	1 M HNO_3
		+1.44	1 M H_2SO_4
		+1.28	1 M HCl
$2HClO + 2H^+ + 2e \rightleftharpoons Cl_2 + 2H_2O$	+1.63		
$NaBiO_3 + 6H^+ + 2e \rightleftharpoons Na^+ + Bi^{3+} + 3H_2O$	+1.6		
$H_5IO_6 + H^+ + 2e \rightleftharpoons IO_3^- + 3H_2O$	+1.6		
$2BrO_3^- + 12H^+ + 10e \rightleftharpoons Br_2 + 6H_2O$	+1.52		
$MnO_4^- + 8H^+ + 5e \rightleftharpoons Mn^{2+} + 4H_2O$	+1.51		
$Mn^{3+} + e \rightleftharpoons Mn^{2+}$	+1.51		
$PbO_2 + 4H^+ + 2e \rightleftharpoons Pb^{2+} + 2H_2O$	+1.455		
$Cl_2 + 2e \rightleftharpoons 2Cl^-$	+1.359		
$Cr_2O_7^{2-} + 14H^+ + 6e \rightleftharpoons 2Cr^{3+} + 7H_2O$	+1.33		
		+1.09	1 M HCl
$MnO_2 + 4H^+ + 2e \rightleftharpoons Mn^{2+} + 2H_2O$	+1.23		
		+1.24	1 M $HClO_4$
$O_2 + 4H^+ + 4e \rightleftharpoons 2H_2O$	+1.229		
$2IO_3^- + 12H^+ + 10e \rightleftharpoons I_2 + 6H_2O$	+1.195		
$Br_{2(aq)} + 2e \rightleftharpoons 2Br^-$	+1.087[a]		
$Br_2(l) + 2e \rightleftharpoons 2Br^-$	+1.065[a]		