DEPARTMENT OF CHEMISTRY

UNIVERSITY OF SWAZILAND

C204 **INTRODUCTION TO ANALYTICAL CHEMISTRY**

MAY 2013 FINAL EXAMINATION

Time Allowed: Three (3) Hours

Instructions:

1. **This examination has six (6) questions and one (1) data sheet. The total number of pages is four (4), including this page.**

2. **Answer any four (4) questions fully; diagrams should be clear, large and properly labeled. Marks will be deducted for improper units and lack of procedural steps in calculations.**

3. **Each question is worth 25 marks.**

Special Requirements

1. **Data sheet.**

2. **Graph paper.**

YOU ARE NOT SUPPOSED TO OPEN THIS PAPER UNTIL PERMISSION TO DO SO HAS BEEN GIVEN BY THE CHIEF INVIGILATOR.

Question 1[25]

(a) It is found from a reliable method that the glucose level in a blood sample is 125 μg/g. You have developed a new method for glucose analysis, and your values for this blood sample are:

117 μg/g	119 μg/g	111 μg/g	115 μg/g	120 μg/g

(i) Is your method significantly different from the reliable one at 95% confidence level? (2)

(ii) Is the value 111 μg/g part of the data set? Explain why (2)

(b) Yet another method has been developed in by another researcher, and the following results are obtained for the sample mentioned above:

135 μg/g	125 μg/g	112 μg/g	122 μg/g	115 μg/g	131 μg/g	119 μg/g

(i) Does your method give the same mean as the one above at 95% confidence level? (2)

(ii) Does your method give the same precision as the one above at 95% confidence level? (2)

(c) For the following calibration,

Protein concentration (μg/g)	0.00	9.36	18.72	28.08	37.44
Titration volume (mL)	4.66	6.76	8.33	10.86	12.80

(i) Use the least squares method to determine the equation of the best straight line (4)

(ii) Draw this line

(d) For diethyl ether with an autoprotolysis constant of 5×10^{-12} as solvent, write down the autoprotolysis equation and calculate the pH of its neutral solutions. (2)

(e) Calculate the pH of 0.55M NH_4Cl given that K_b for ammonia is 1.76×10^{-5} (3)

(f) Calculate the fraction dissociated in (e) above (2)

(g) Explain how you would prepare 500mL of a pH 8.64 buffer solution from solid NH_4Cl and a commercial solution that is 67% v/v NH_3 and density 1.24 g/mL. (5)

Question 2[25]

(a) (i) Briefly describe how dichlorofluorescein functions as an indicator in the Fajan's precipitation titration. (3)

(ii) In the determination of chloride ion in waste water, explain why dextrin is added to the solution prior to the Fajans titration. (1)

(b) Describe the mechanism of formation of a precipitate in gravimetric analysis. (3)

(c) Using diagrams discuss the two impurity formation process of "occlusion" and "adsorption" in gravimetric analysis. (4)

(d) With regards to the Mohr Method in precipitation titrations:

(i) Use chemical equations to explain how the end point is detected. (3)

(ii) Use chemical equations to explain how low pH conditions result in titration errors, and how are these eliminated. (2)

(iii) Explain why the concentration of indicator is critical in reducing indicator concentration induced errors. (2)

(e) With regards to the Volhard Method in precipitation titrations:

(i) Use chemical equations to explain how the end point is detected. (3)

(ii) Use chemical equations to explain why over time the indicator changes colour to the original titrant colour. (2)

(iii) Describe two ways in which the error resulting in (ii) above is eliminated. (2)

Question 3[25]

(a) For benzoic acid C_6H_5COOH as solvent,

(i) Write down a chemical equation depicting autoprotolysis (2)

(ii) Calculate the pH of its "neutral" solutions given that the autoprotolysis constant is 4.5×10^{-6} at $25^{0}C$. (3)

(b) In acid-base titrimetry,

(i) State two reasons why is NaOH not a sutable primary standard (2)

(ii) Name a common primary standard for the standardization of NaOH (2)

(c) Draw the chemical structure of thymol blue, and explain why this indicator is able to be used over a very wide pH range covering acidic and basic titrations. (4)

(d) Using phenolphthalein as indicator (pink in basic solution but colourless in acid),

(i) Derive the Henderson – Hasselbach equation for phenolphthalein (3)

(ii) Given that the Ka of phenolphthalein is 1×10^{-9} use the Henderson equation to derive the useful pH range for the indicator. (4)

(iii) Plot the titration curve expected from titration of 50ml of 0.02M KOH with 0.100M HBr, using the following data points. (5)

0.00 ml added 5.00 ml added 9.99 ml added 10.01 ml added 16.00 ml added

Question 4[25]

(a) In complexometric titrations,

(i) What does the acronym "DPTA" stand for, and draw its chemical structure (3)

(ii) Use an example to explain the term " Multidentate" ligand (3)

(iii) For the titration of Mg^{2+} in the presence of Al^{3+}, excess fluoride is usually added at pH = 10. Explain why (3)

(b) Use an equation to explain what a condtional formation constant is in complexometric titrations. (3)

(c) Calculate the concentration of free Fe^{3+} in solutions of 0.10M $Fe(EDTA)^-$ at pH = 8.00. (4)

(d) Draw the chemical structure of Eriochrome Black T, and explain how this indicator works in EDTA titrations. (4)

(e) A 0.100 M EDTA solution is used to titrate 25ml of 0.050ml of 0.050M Mg^{2+} buffered at pH = 10 using Eriochrome Black T as indicator.

(i) Calculate the pMg after addition of the following volumes of EDTA: (4)

2 mL 12 mL 12.5 mL 13 mL

(ii) Plot the titration curve. (1)

Question 5[25]

(a) What does the acronym "redox" stand for? (1)

(b) For the electrochemical cell:

Cd (s) | $CdCl_2$ (aq, 0.0538M) || $AgNO_3$ (aq, 0.0328M) | Ag (s)

(i) What component is represented by the symbol "||"? Explain how it works and why the component is used in electrochemical titrations. (5)

(ii) Would the cell be galvanic as written? (5)

(c) In the iodometric determination of cooper using thiosulfate as titrant,

(i) Name a suitable primary standard (1)

(ii) Name a most widely used specific indicator for the titration (1)

(iii) Explain the role of ammonium bifloride added to the samples prior to titration (2)

(iv) Explain why the indicator named in c (ii) above is added just before the end point is reached and not at the beginning of the titration (3)

(v) Use chemical equations to illustrate how this acts as an indicator for this titration. (3)

(d) A titration is carried out in a cell, whereby the potential vs SCE (0.241V) is measured for a 25 ml solution of 0.020 M Cr^{2+} (E^0 = -0.41) titrated with 0.010M Fe^{3+} (E^0 = 0.770).

(i) Calculate the potential (vs SCE) after addition of the following volumes during the titration (3)

5.00 ml 50.00 ml 100 ml

(ii) Sketch the titration curve (1)

Question 6[25]

(a) Given that at 20 ^{0}C only 0.24 g of an organic acid A dissolves in 100 mL of water, but 2.70 g of the same acid dissolves in 100 mL of ether, calculate the value of the partition coefficient. (4)

(b) Using diagrams, explain how single stage solvent extraction works. (4)

(c) List and describe any four (4) properties to be considered in the selection of an organic solvent for extraction. (4)

(d) List three elements which form stable chloro complexes which are appreciably soluble in organic solvents and used to separate these elements from complex matrices (3)

(e) Describe two ways of recovering analytes from organic solvent during the stripping stage of solvent extraction. (4)

(f) Metal chloro complex MCl_3 is extremely soluble in ether, the distribution coefficient for a water/ether system being 50. Calculate the concentration of MCl_3 left in 50ml of aqueous 0.01 M $FeCl_3$ solution after extraction

(i) once with a 10 ml portion of ether (2)

(ii) once with a 20 ml portion of ether (2)

(iii) twice with 10 ml portion of ether (2)

1. PERIODIC CHART OF THE ELEMENTS

1 1A	2 2A	3 3B	4 4B	5 5B	6 6B	7 7B	8 8B	9 8B	10 8B	11 1B	12 2B	13 3A	14 4A	15 5A	16 6A	17 7A	18
								1 H 1.00794									2 He 4.00260
3 Li 6.941	4 Be 9.01218											5 B 10.81	6 C 12.011	7 N 14.0067	8 O 15.9994	9 F 18.99840	10 Ne 20.179
11 Na 22.98977	12 Mg 24.305											13 Al 26.98154	14 Si 28.0855	15 P 30.97376	16 S 32.06	17 Cl 35.453	18 Ar 39.948
19 K 39.0983	20 Ca 40.08	21 Sc 44.9559	22 Ti 47.88	23 V 50.9415	24 Cr 51.996	25 Mn 54.9380	26 Fe 55.847	27 Co 58.9332	28 Ni 58.69	29 Cu 63.546	30 Zn 65.38	31 Ga 69.72	32 Ge 72.59	33 As 74.9216	34 Se 78.96	35 Br 79.904	36 Kr 83.80
37 Rb 85.4678	38 Sr 87.62	39 Y 88.9059	40 Zr 91.22	41 Nb 92.9064	42 Mo 95.94	43 Tc (98)	44 Ru 101.07	45 Rh 102.9055	46 Pd 106.42	47 Ag 107.8682	48 Cd 112.41	49 In 114.82	50 Sn 118.69	51 Sb 121.75	52 Te 127.60	53 I 126.9045	54 Xe 131.29
55 Cs 132.9054	56 Ba 137.33	57 ★ La 138.9055	72 Hf 178.49	73 Ta 180.9479	74 W 183.85	75 Re 186.207	76 Os 190.2	77 Ir 192.22	78 Pt 195.08	79 Au 196.9665	80 Hg 200.59	81 Tl 204.383	82 Pb 207.2	83 Bi 208.9804	84 Po (209)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra 226.0254	89 ▲ Ac 227.0278	104 Unq (261)	105 Unp (262)	106 Unh (263)	107 Uns (262)	108 Uno (265)	109 Une (266)									

A value in brackets denotes the mass number of the longest lived or best known isotope.

Series														
★ Lanthanide series	58 Ce 140.12	59 Pr 140.9077	60 Nd 144.24	61 Pm (145)	62 Sm 150.36	63 Eu 151.96	64 Gd 157.25	65 Tb 158.9254	66 Dy 162.50	67 Ho 164.9304	68 Er 167.26	69 Tm 168.9342	70 Yb 173.04	71 Lu 174.967
▲ Actinide series	90 Th 232.0381	91 Pa 231.0359	92 U 238.0289	93 Np 237.0482	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (260)

4. NET STABI[LITY] CONSTANT[S]

$Ag(CN)_2^-$	5
$Ag(NH_3)_2^+$	1.6
$Ag(S_2O_3)_2^{-3}$	4.7
$Al(OH)_4^-$	1.0
$Ca(EDTA)^=$	1.0
$Cd(CN)_4^=$	8.3
$Cd(NH_3)_4^{++}$	5.5
$Co(NH_3)_6^{+3}$	2
$Cr(OH)_4^-$	4
$Cu(CN)_4^{-3}$	1
$Cu(NH_3)_4^{++}$	1.2
$Fe(CN)_6^{-3}$	4.0
$Fe(CN)_6^{-4}$	2.5
$Fe(SCN)^{++}$	1.0
$HgCl_4^=$	1.3
$Hg(CN)_4^=$	8.3
$Hg(SCN)_4^=$	5.0
$HgI_4^=$	6.3
$Mg(EDTA)^=$	1.3
$Ni(NH_3)_4^{++}$	4.7
$Pb(OH)_3^-$	7.9
$Zn(CN)_4^=$	4.2
$Zn(NH_3)_4^{++}$	7.8
$Zn(OH)_4^=$	6.3

2. IONIZATION CONSTANTS (K_A) FOR WEAK ACIDS

Acid		K_A
Acetic		1.9×10^{-5}
2-Amino-pyridinium Ion		2×10^{-7}
Ammonium Ion		5.6×10^{-10}
Anilinium Ion		2.3×10^{-5}
Arsenic	K_1	5.6×10^{-3}
Benzoic		6.7×10^{-5}
Boric	K_1	5×10^{-10}
Carbonic	K_1	4.3×10^{-7}
	K_2	5.6×10^{-11}
Chloroacetic		1.5×10^{-3}
Chromic	K_2	3.2×10^{-7}
Citric	K_1	8.7×10^{-4}
	K_2	1.8×10^{-5}
	K_3	4×10^{-6}
Dichloroacetic		5×10^{-2}
EDTA	K_1	7×10^{-3}
	K_2	2×10^{-3}
	K_3	7×10^{-7}
	K_4	6×10^{-11}
Formic		2×10^{-4}
α-D(+)-Glucose		5.2×10^{-13}
Glycinium Ion	K_1	4.6×10^{-3}
	K_2	2.5×10^{-10}
Hydrazinium Ion		5.9×10^{-9}
Hydrocyanic		7×10^{-10}
Hydrofluoric		7×10^{-4}
Hydroxyl-ammonium Ion		9.1×10^{-7}
Hypochlorous		3.7×10^{-8}
H_2S	K_1	9×10^{-8}
	K_2	1×10^{-15}
Imidazolium Ion		1.1×10^{-7}
Lactic		1.4×10^{-4}
Methylammonium Ion		2.7×10^{-11}
Monoethanol-ammonium Ion		3×10^{-10}
Nicotinium Ion		9.6×10^{-9}
Oxalic	K_1	6×10^{-2}
	K_2	6×10^{-5}
Phenol		1.3×10^{-10}
Phthalic	K_2	4×10^{-6}
Phosphoric	K_1	7.5×10^{-3}
	K_2	6.2×10^{-8}
	K_3	4.7×10^{-13}
Phosphorous	K_1	1.0×10^{-2}
	K_2	2.6×10^{-7}
Pyridinium Ion		1×10^{-5}
Succinic	K_1	7×10^{-5}
	K_2	2.5×10^{-6}
Sulfuric	K_2	1.2×10^{-2}
Sulfurous	K_1	2×10^{-2}
	K_2	6×10^{-8}
Trimethyl-ammonium Ion		1.6×10^{-10}
Uric		1.3×10^{-4}
Water, K_w, 24°C		1.0×10^{-14}

3. SOLUBILITY PRODUCT CONSTANTS

AgBr	4×10^{-13}	BaC_2O_4	2×10^{-8}	$KClO_4$	2×10^{-2}
Ag_2CO_3	6×10^{-12}	$BaSO_4$	1×10^{-10}	$MgCO_3$	1×10^{-5}
AgCl	1×10^{-10}	$CaCO_3$	5×10^{-9}	MgC_2O_4	9×10^{-5}
Ag_2CrO_4	2×10^{-12}	CaF_2	4×10^{-11}	$MgNH_4PO_4$	2×10^{-13}
$Ag[Ag(CN)_2]$	4×10^{-12}	CaC_2O_4	2×10^{-9}	$Mg(OH)_2$	1×10^{-11}
AgI	1×10^{-16}	CdS	1×10^{-28}	MnS	1×10^{-15}
Ag_3PO_4	1×10^{-19}	$Cu(OH)_2$	2×10^{-20}	$PbCrO_4$	2×10^{-14}
Ag_2S	1×10^{-50}	CuS	1×10^{-36}	PbS	1×10^{-28}
AgCNS	1×10^{-12}	$Fe(OH)_3$	1×10^{-36}	$PbSO_4$	2×10^{-8}
$Al(OH)_3$	2×10^{-32}	Hg_2Br_2	3×10^{-23}	$SrCrO_4$	4×10^{-5}
$BaCO_3$	5×10^{-9}	Hg_2Cl_2	6×10^{-19}	$Zn(OH)_2$	3.6×10^{-16}
$BaCrO_4$	1×10^{-10}	HgS	1×10^{-52}	ZnS	1×10^{-24}

5. FIRST IONIZATION ENERGIES, e.v

H: 14

1A	2A	3B	4B	5B	6B	7B	8B	8B	8B	1B	2B	3A	4A	5A	6A
5.4	9.3											8.3	11	15	14
5.1	7.6											6.0	8.1	11	10
4.3	6.1	6.6	6.8	6.7	6.8	7.4	7.9	7.9	7.6	7.7	9.4	6.0	8.1	10	9.8
4.2	5.7	6.6	7.0	6.8	7.2		7.5	7.7	8.3	7.6	9.0	5.8	7.3	8.6	9.0
3.9	5.2	5.0 6.9	5.5	6	8.0	7.9	8.7	9.2	9.0	9.2	10	6.1	7.4	8	

6. ELECTRONEGATIVITIES, Pauling

H: 2.1

1A	2A	3B	4B	5B	6B	7B	8B	8B	8B	1B	2B	3A	4A	5A	6A
1.0	1.5											2.0	2.5	3.0	3.5
0.9	1.2											1.5	1.8	2.1	2.5
0.8	1.0	1.3	1.5	1.6	1.6	1.5	1.8	1.8	1.8	1.9	1.6	1.8	1.8	2.0	2.4
0.8	1.0	1.2	1.4	1.6	1.8	1.9	2.2	2.2	2.2	1.9	1.7	1.7	1.8	1.9	2.1
0.7	0.9	1.1	1.3	1.5	1.7	1.9	2.2	2.2	2.2	2.4	1.9	1.8	1.8	1.9	2.0

7. ATOMIC RADII picometers

H: 37

1A	2A	3B	4B	5B	6B	7B	8B	8B	8B	1B	2B	3A	4A	5A	6A
155	112											98	91	92	73
190	160											143	132	128	127
235	197	162	147	134	130	135	126	125	124	128	138	141	137	139	140
248	215	178	160	146	139	136	134	134	137	144	154	166	162	159	160
267	222	187	167	149	141	137	135	136	139	146	157	171	175	170	176

8. IONIC RADII pm

Li^+	60	Sr^{+2}	113	S^{-2}	184
Na^+	95	Ba^{+2}	135	Se^{-2}	198
K^+	133	B^{+3}	20	Te^{-2}	221
Rb^+	148	Al^{+3}	50	F^-	136
Be^{+2}	31	N^{+3}	171	Cl^-	181
Mg^{+2}	65	P^{+3}	212	Br^-	195
Ca^{+2}	99	O^{-2}	140	I^-	216

9. LATTICE ENER[GIES]

(All negative)

	F	Cl	Br
Li	1030	840	78
Na	914	770	72
K	812	701	67
Rb	780	682	65
Cs	744	630	61

10. HALF LIVES

H^3	12.3 years	K^{40}	1.28×10^9y	I^{131}	8.1
F^{20}	11.4 secs	Ca^{45}	165 days	Cs^{137}	30
C^{14}	5730 years	Fe^{59}	45 days	Au^{198}	2.69
Na^{24}	15.0 hours	Co^{60}	5.26 y	Ra^{226}	162
P^{32}	14.3 days	Br^{82}	35.5 hours	U^{235}	7.1 ×
S^{35}	88 days	Sr^{90}	28 years	U^{238}	4.51×
Cl^{36}	3.1×10^5y	I^{129}	1.7×10^7y	Pu^{230}	24,

 University of Alberta, Edmonton Printed in Canada

Table 26-5 VALUES OF F AT THE 95% CONFIDENCE LEVEL

ν_2	ν_1: 2	3	4	5	6	∞
2	19.00	19.16	19.25	19.30	19.33	19.50
3	9.55	9.28	9.12	9.01	8.94	8.53
4	6.94	6.59	6.39	6.26	6.16	5.63
5	5.79	5.41	5.19	5.05	4.95	4.36
6	5.14	4.76	4.53	4.39	4.28	3.67
∞	3.00	2.60	2.37	2.21	2.10	1.00

Table 4-2
Values of Student's t

Degrees of freedom	Confidence level (%): 50	80	90	95	99
1	1.000	3.078	6.314	12.706	63.657
2	0.816	1.886	2.920	4.303	9.925
3	0.765	1.638	2.353	3.182	5.841
4	0.741	1.533	2.132	2.776	4.604
5	0.727	1.476	2.015	2.571	4.032
6	0.718	1.440	1.943	2.447	3.707
7	0.711	1.415	1.895	2.365	3.500
8	0.706	1.397	1.860	2.306	3.355
9	0.703	1.383	1.833	2.262	3.250
10	0.700	1.372	1.812	2.228	3.169
15	0.691	1.341	1.753	2.131	2.947
20	0.687	1.325	1.725	2.086	2.845
∞	0.674	1.282	1.645	1.960	2.576

Table 4-4
Values of Q for rejection of data

Q (90% confidence)	0.94	0.76	0.64	0.56	0.51	0.47	0.44	0.41
Number of observations	3	4	5	6	7	8	9	10

ACID-BASE INDICATORS

Indicator	pH range	pKin	Acid	Base
Thymol blue	1.2 – 2.8	1.6	red	yellow
Methyl yellow	2.9 – 4.0	3.3	red	yellow
Methyl orange	3.1 – 4.4	4.2	red	yellow
Bromocresol green	3.8 – 5.4	4.7	yellow	blue
Methyl red	4.2 – 6.2	5.0	red	yellow
Chlorophenol red	4.8 – 6.4	6.0	yellow	red
Bromothymol blue	6.0 – 7.6	7.1	yellow	blue
Phenol red	6.4 – 8.0	7.4	yellow	red
Cresol purple	7.4 – 9.0	8.3	yellow	purple
Thymol blue	8.0 – 9.6	8.9	yellow	blue
Phenolphthalein	8.0 – 9.8	9.7	colorless	red
Thymolphthalein	9.3 – 10.5	9.9	colorless	blue

n	Q_{90}	n	Q_{90}	n	Q_{90}
3	0.94	6	0.56	9	0.44
4	0.76	7	0.51	10	0.41
5	0.64	8	0.47		

15. Bond Enthalpies

$kJ\ mol^{-1}$ at 25°C (i.e. Bond Energies)

Single	O	N	C	S	F	Cl
H	463	391	413	368	563	432
C	358	305	346	272	489	328
N	222	163			275	192

MISC.

S—S 251	H—H 436	C=C 615
S—F 327	N≡N 946	C≡C 812
S—Cl 271	N=O 607	C=O 749

D.F.	t_{50}	t_{90}
1	1.0	6.3
2	0.82	2.9
3	0.76	2.35
4	0.74	2.13
5	0.73	2.02
6	0.72	1.94
7	0.71	1.90
8	0.71	1.86
9	0.70	1.83
10	0.70	1.81
20	0.69	1.72
30	0.68	1.70
∞	0.67	1.64

12. ELECTRODE POTENTIALS, $\mathcal{E}°$

$Na^+ + e \rightleftharpoons Na$	−2.713
$Mg^{++} + 2e \rightleftharpoons Mg$	−2.37
$Al^{+++} + 3e \rightleftharpoons Al$	−1.66
$Zn^{++} + 2e \rightleftharpoons Zn$	−0.763
$Fe^{++} + 2e \rightleftharpoons Fe$	−0.44
$Cd^{++} + 2e \rightleftharpoons Cd$	−0.403
$Cr^{+++} + e \rightleftharpoons Cr^{++}$	−0.38
$Tl^+ + e \rightleftharpoons Tl$	−0.336
$V^{+++} + e \rightleftharpoons V^{++}$	−0.255
$Sn^{++} + 2e \rightleftharpoons Sn$	−0.14
$Pb^{++} + 2e \rightleftharpoons Pb$	−0.126
$2H^+ + 2e \rightleftharpoons H_2$	0.000
$S_4O_6^{=} + 2e \rightleftharpoons 2S_2O_3^{=}$	0.09
$TiO^{++} + 2H^+ + e \rightleftharpoons Ti^{+++} + H_2O$	0.10
$S + 2H^+ + 2e \rightleftharpoons H_2S$	0.14
$Sn^{+4} + 2e \rightleftharpoons Sn^{++}$	0.14
$Cu^{++} + e \rightleftharpoons Cu^+$	0.17
$SO_4^{=} + 4H^+ + 2e \rightleftharpoons H_2O + H_2SO_3$	0.17
$AgCl + e \rightleftharpoons Cl^- + Ag$	0.222
Saturated calomel	(0.244)
$Hg_2Cl_2 + 2e \rightleftharpoons 2Cl^- + 2Hg$	0.268
$Bi^{+++} + 3e \rightleftharpoons Bi$	0.293
$UO_2^{++} + 4H^+ + 2e \rightleftharpoons U^{+4} + 2H_2O$	0.33
$VO^{++} + 2H^+ + e \rightleftharpoons V^{+++} + H_2O$	0.34
$Cu^{++} + 2e \rightleftharpoons Cu$	0.34
$Fe(CN)_6^{-3} + e \rightleftharpoons Fe(CN)_6^{-4}$	0.355
$Cu^+ + e \rightleftharpoons Cu$	0.52
$I_3^- + 2e \rightleftharpoons 3I^-$	0.545
$H_3AsO_4 + 2H^+ + 2e \rightleftharpoons H_3AsO_3 + H_2O$	0.56
$I_2 + 2e \rightleftharpoons 2I^-$	0.621
$2HgCl_2 + 2e \rightleftharpoons Hg_2Cl_2 + 2Cl^-$	0.63
$O_2 + 2H^+ + 2e \rightleftharpoons H_2O_2$	0.69
Quinone + $2H^+ + 2e \rightleftharpoons$ Hydroquinone	0.70
$Fe^{+++} + e \rightleftharpoons Fe^{++}$	0.771
$Hg_2^{++} + 2e \rightleftharpoons 2Hg$	0.792
$Ag^+ + e \rightleftharpoons Ag$	0.799
$Hg^{++} + 2e \rightleftharpoons Hg$	0.851
$2Hg^{++} + 2e \rightleftharpoons Hg_2^{++}$	0.907
$NO_3^- + 3H^+ + 2e \rightleftharpoons HNO_2 + H_2O$	0.94
$HNO_2 + H^+ + e \rightleftharpoons NO + H_2O$	0.98
$VO_2^+ + 2H^+ + e \rightleftharpoons VO^{++} + H_2O$	0.999
$Br_2 + 2e \rightleftharpoons 2Br^-$	1.08
$2IO_3^- + 12H^+ + 10e \rightleftharpoons 6H_2O + I_2$	1.19
$O_2 + 4H^+ + 4e \rightleftharpoons 2H_2O$	1.229
$MnO_2 + 4H^+ + 2e \rightleftharpoons Mn^{++} + 2H_2O$	1.23
$Cr_2O_7^{=} + 14H^+ + 6e \rightleftharpoons 7H_2O + 2Cr^{+++}$	1.33
$Cl_2 + 2e \rightleftharpoons 2Cl^-$	1.358
$2BrO_3^- + 12H^+ + 10e \rightleftharpoons 6H_2O + Br_2$	1.50
$MnO_4^- + 8H^+ + 5e \rightleftharpoons 4H_2O + Mn^{++}$	1.51
$Ce^{+4} + e \rightleftharpoons Ce^{+3}$	1.61

13. MEAN ACTIVITY COEFFICIENTS

M	KCl	Na_2SO_4	$ZnSO_4$
0.001	0.965	0.89	0.70
0.01	0.901	0.72	0.39
0.1	0.769	0.45	0.15

16. HEATS OF FORMATION

$\Delta H°$ in $kJ\ mol^{-1}$ at 25°C
All ions in H_2O solution except as noted
All Elements = 0

H_g	218	H^+	0.0	H_2O_g	−242
O_g	249	Na^+	−240	H_2O_l	−286
C_g	717	Ag^+	106	CO_g	−111
N_g	473	NH_4^+	−133	CO_{2g}	−394
F_g	79	OH^-	−230	NH_{3g}	−46
Cl_g	122	F^-	−333	NO_g	90
Br_g	112	Cl^-	−167	NO_{2g}	33
I_g	107	Br^-	−122	N_2O_{4g}	9
S_g	279	I^-	−55	SO_{2g}	−297
P_g	315	$S^=$	33	SO_{3g}	−396
Na_g	107	$SO_4^=$	−909	H_2S_g	−21
K_g	88	$CO_3^=$	−677	NaF_s	−574
Na^+_g	609	HF_g	−271	$NaCl_s$	−411
K^+_g	514	HCl_g	−92	KF_s	−567
F^-_g	−255	HBr_g	−36	KCL_s	−437
Cl^-_g	−233	HI_g	26	$AgCl_s$	−127
CH_{4g}	−75	HCN_g	135	$AgBr_s$	−100
C_2H_{2g}	227	PH_{3g}	5	PCl_{3g}	−287
C_2H_{4g}	52	C_6H_{6l}	49	PCl_{5g}	−375
C_2H_{6g}	−85	CH_3OH_l	−238		
C_3H_{8g}	−105	$C_2H_5OH_g$	−235		
nC_4H_{10g}	−127	$C_2H_5OH_l$	−278		
nC_8H_{18g}	−209	$COCl_{2g}$	−219		
CCl_{4l}	−135	CH_3Cl_g	−81		

17. ABS. ENTROPY S°

$J\ mol^{-1}\ K^{-1}$, at 25°C

H_{2g}	131	P_{4wh}	164	SF_{6g}	292
N_{2g}	192	HF_g	174	NO_g	211
O_{2g}	205	HCl_g	187	NO_{2g}	240
Cl_{2g}	223	H_2O_g	189	N_2O_{4g}	304
F_{2g}	203	CO_g	198	NH_{3g}	192
Cgra	5.7	CO_{2g}	214	PCl_{3g}	312
S_{8r}	254	SO_{2g}	248	PCl_{5g}	365
CH_{4g}	186	SO_{3g}	256	BF_{3g}	254
C_2H_{6g}	229	CH_3OH_l	127		
C_3H_{8g}	270	$C_2H_5OH_g$	283		
C_2H_{2g}	201	$C_2H_5OH_l$	161		
C_2H_{4g}	219	$(CH_3)_2O_g$	266		
C_6H_{6g}	269	CH_3COOH_g	282		

18. $\Delta G°$ FORMATION

$kJ\ mol^{-1}$ at 25°C

H_g	203	HF_g	−273	H_2O_g	−229
F_g	62	HCl_g	−95	H_2O_l	−237
Cl_g	106	HBr_g	−54	SO_{2g}	−300
O_g	232	HI_g	1.7	SO_{3g}	−371
NO_g	87	NH_{3g}	−16	PCl_{3g}	−268
NO_{2g}	51	CO_g	−137	PCl_{5g}	−305
N_2O_{4g}	98	CO_{2g}	−394	CH_{4g}	−51
C_2H_{4g}	68	C_2H_{2g}	209	C_2H_{6g}	−33
C_6H_{6l}	125	CH_3OH_l	−162		
CCl_{4l}	−65	$C_2H_5OH_l$	−175		
BF_{3g}	−1120	$CHCl_{3g}$	−70		
SF_{6g}	−1105	CH_3COOH_g	−374		

20. CONC. ACIDS AN

	M.W.	Density	W
Acetic	60.05	1.05	9
H_2SO_4	98.07	1.83	9
HF	20.01	1.14	4
HCl	36.46	1.19	3
HBr	80.91	1.52	4
HNO_3	63.01	1.41	6
$HClO_4$	100.46	1.67	7
H_3PO_4	98.00	1.69	8
NaOH	40.00	1.53	5
NH_3	17.03	0.90	2

21. DENSITIES (g

Water at		Air (70 cm
0_s°C	0.9168	Glass
10°	0.9997	Na_2CO_3
20°	0.9982	NaCl
22°	0.9978	$BaSO_4$
24°	0.9973	AgCl
26°	0.9968	Aluminum
28°	0.9963	Iron
30°	0.9956	Brass
90°	0.9653	Mercury
100_g°	0.0006	Platinum

22. MOBILITIES ($m^2V^{-1}s$

Li^+	39	H_3O^+	350
Na^+	50	NH_4^+	73
K^+	74	Ag^+	62
Cl^-	76	OH^-	198
Br^-	78	I^-	77

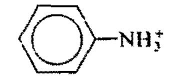
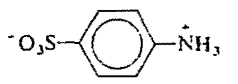
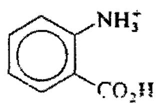
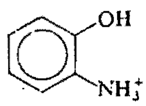
23. WATER V.P. (to

0°C	4.6
15°	12.8
20°	17.5

24. MISCELLANE

Std. dev. = $\sqrt{\Sigma(X_i - \bar{X})^2/($
Conf. limits = $\bar{X} \pm ts/\sqrt{n}$
$E = E° - (0.0592/n)\log([Red]/$
$\log I_o/I_t = abc = A = \log 1/$
$\log N_T = \log N_0 - 0.301T/T_{\frac{1}{2}}$
$x = (-b \pm \sqrt{b^2 - 4ac})/2a$
$n\lambda = 2d \sin\theta$
$2.303 \log_{10} a = \log_e a$
$h = 6.626 \times 10^{-34}\ J\ s$
$e = 1.602 \times 10^{-19}\ C$
$N_A = 6.022 \times 10^{23}\ mol^{-1}$
F = 96487 C
$g = 9.807\ m\ s^{-2}$
$c = 2.998 \times 10^8\ m\ s^{-1}$
$1\ amu = 1.661 \times 10^{-27}\ kg$
$R = 1.987\ cals\ mol^{-1}\ K^{-1}$
$= 0.08206$ litre atm mol
$= 8.314\ J\ mol^{-1}\ K^{-1}$
$= 8.314\ kPa\ dm^3\ mol^{-1}$
0 °C = 273.15 K
$1\ eV = 1.602 \times 10^{-19}\ J$
1 cal = 4.1840 J

G / Acid Dissociation Constants

Name	Structure[†]	pK_a[‡]	K_a
Acetic acid (ethanoic acid)	CH_3CO_2H	4.757	1.75×10^{-5}
Alanine	$\overset{NH_3^+}{\underset{CO_2H}{CHCH_3}}$	2.348 (CO_2H) 9.867 (NH_3)	4.49×10^{-3} 1.36×10^{-10}
Aminobenzene (aniline)		4.601	2.51×10^{-5}
4-Aminobenzenesulfonic acid (sulfanilic acid)		3.232	5.86×10^{-4}
2-Aminobenzoic acid (anthranilic acid)		2.08 (CO_2H) 4.96 (NH_3)	8.3×10^{-3} 1.10×10^{-5}
2-Aminoethanethiol (2-mercaptoethylamine)	$HSCH_2CH_2NH_3^+$	8.21 (SH) ($\mu = 0.1$) 10.71 (NH_3) ($\mu = 0.1$)	6.2×10^{-9} 1.95×10^{-11}
2-Aminoethanol (ethanolamine)	$HOCH_2CH_2NH_3^+$	9.498	3.18×10^{-10}
2-Aminophenol		4.78 (NH_3) (20°) 9.97 (OH) (20°)	1.66×10^{-5} 1.05×10^{-10}
Ammonia	NH_4^+	9.244	5.70×10^{-10}
Arginine	NH_3^+–$CH(CO_2H)CH_2CH_2CH_2NHC(=NH_2^+)NH_2$	1.823 (CO_2H) 8.991 (NH_3) (12.48) (NH_2)	1.50×10^{-2} 1.02×10^{-9} 3.3×10^{-13}
Arsenic acid (hydrogen arsenate)	HO–As(=O)(OH)–OH	2.24 6.96 11.50	5.8×10^{-3} 1.10×10^{-7} 3.2×10^{-12}

[†] Each acid is written in its protonated form. The acidic protons are indicated in bold type.
[‡] pK_a values refer to 25°C and zero ionic strength unless otherwise indicated. Values in parentheses are considered to be less reliable. Data are from A. E. Martell and R. M. Smith, *Critical Stability Constants* (New York: Plenum Press, 1974).

N = 14.01 Cl = 35.45 H = 1.0079

Values of $\alpha_{Y^{4-}}$ for EDTA at 20°C and $\mu = 0.10$ M

pH	$\alpha_{Y^{4-}}$
0	1.3×10^{-23}
1	1.9×10^{-18}
2	3.3×10^{-14}
3	2.6×10^{-11}
4	3.8×10^{-9}
5	3.7×10^{-7}
6	2.3×10^{-5}
7	5.0×10^{-4}
8	5.6×10^{-3}
9	5.4×10^{-2}
10	0.36
11	0.85
12	0.98
13	1.00
14	1.00

Table 14-2
Formation constants for metal–EDTA complexes

Ion	log K_f	Ion	log K_f	Ion	log K_f
Li^+	2.79	Mn^{3+}	25.3 (25°C)	Ce^{3+}	15.98
Na^+	1.66	Fe^{3+}	25.1	Pr^{3+}	16.40
K^+	0.8	Co^{3+}	41.4 (25°C)	Nd^{3+}	16.61
Be^{2+}	9.2	Zr^{4+}	29.5	Pm^{3+}	17.0
Mg^{2+}	8.79	Hf^{4+}	29.5 ($\mu = 0.2$)	Sm^{3+}	17.14
Ca^{2+}	10.69	VO^{2+}	18.8	Eu^{3+}	17.35
Sr^{2+}	8.73	VO_2^+	15.55	Gd^{3+}	17.37
Ba^{2+}	7.86	Ag^+	7.32	Tb^{3+}	17.93
Ra^{2+}	7.1	Tl^+	6.54	Dy^{3+}	18.30
Sc^{3+}	23.1	Pd^{2+}	18.5 (25°C, $\mu = 0.2$)	Ho^{3+}	18.62
Y^{3+}	18.09			Er^{3+}	18.85
La^{3+}	15.50			Tm^{3+}	19.32
V^{2+}	12.7	Zn^{2+}	16.50	Yb^{3+}	19.51
Cr^{2+}	13.6	Cd^{2+}	16.46	Lu^{3+}	19.83
Mn^{2+}	13.87	Hg^{2+}	21.7	Am^{3+}	17.8 (25°C)
Fe^{2+}	14.32	Sn^{2+}	18.3 ($\mu = 0$)	Cm^{3+}	18.1 (25°C)
Co^{2+}	16.31	Pb^{2+}	18.04	Bk^{3+}	18.5 (25°C)
Ni^{2+}	18.62	Al^{3+}	16.3	Cf^{3+}	18.7 (25°C)
Cu^{2+}	18.80	Ga^{3+}	20.3	Th^{4+}	23.2
Ti^{3+}	21.3 (25°C)	In^{3+}	25.0	U^{4+}	25.8
V^{3+}	26.0	Tl^{3+}	37.8 ($\mu = 1.0$)	Np^{4+}	24.6 (25°C, $\mu = 1.0$)
Cr^{3+}	23.4	Bi^{3+}	27.8		

Note: The stability constant is the equilibrium constant for the reaction $M^{n+} + Y^{4-} \rightleftharpoons MY^{n-4}$. Values in table apply at 20°C and ionic strength 0.1 M, unless otherwise noted.

SOURCE: Data from A. E. Martell and R. M. Smith, *Critical Stability Constants*, Vol. 1 (New York: Plenum Press, 1974), pp. 204–211.