DEPARTMENT OF CHEMISTRY

UNIVERSITY OF SWAZILAND

C204 **INTRODUCTION TO ANALYTICAL CHEMISTRY**

JULY 2013 SUPPLEMENTARY EXAMINATION

Time Allowed: Three (3) Hours

Instructions:

1. **This examination has six (6) questions. The total number of pages is five (5), 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.**

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Question 1[25]

(a) A new microwave method for the analysis of carbon dioxide is being evaluated by comparing the results obtained using it with that of the standard method. The results of the concentrations of the gas (in μL/ m^3), by the two methods are as shown in the Table below:

Standard Method	Microwave Method
216	215
242	223
216	215
235	213
231	257
243	246

(i) Calculate the pooled standard deviation from the two data sets (2)

(ii) Employ the paired t-test to determine whether there is a significant difference between the two methods at the 95% confidence Level. (3)

(iii) Comment on the precision of the microwave method relative to the standard one at 95% confidence level. (2)

(b) For random errors:

(i) Draw the Gaussian curve (2)

(ii) Indicate clearly the position of 1σ (2)

(iii) Indicate clearly the position of μ (1)

(iv) Write down the equation that describes the curve, and explain all terms appearing in it (3)

(c) Of the standardization data set for NaOH solution:

0.5365 M 0.5295 M 0.5466 M 0.5344 M 0.5545 M 0.5366 M

(i) Calculate the coefficient of variation (2)

(ii) Would the data point 0.5545 be considered an outliar at the 90% confidence level? (3)

(iii) If the standardized solution in (v) above yielded the following results for alkalinity of waste water in 4 subsamples as follows:

53.55 mg/mL 54.21 mg/mL 49.65 mg/mL 50.22 mg/mL

Calculate the error due to the subsampling the waste water in mg/mL (5)

Question 2 [25]

(a) For ethanol, CH_3CH_2OH, as a non-aqueous solvent, write down the:

(i) Autoprotolysis equation. (1)
(ii) Expression for the equilibrium constant for autoprotolysis. (1)
(iii) Calculate the pH of a "neutral" solution, given that the autoprotolysis constant is 5×10^{-16}. (2)

(b) (i) Calculate the pH of a 400-mL buffer solution containing 0.200 M NH_3 and 0.300M NH_4Cl (2)
(ii) Calculate the change in pH of the buffer system in b(i) above upon addition of 100 mL of 0.05 M HCl (4)

(c) (i)A 0.1000 M solution of HCl is used to titrate 25.00 ml of 0.0100M $Ba(OH)_2$. Calculate the pH at the following volumes of HCl added during that titration (5)

2.00 ml, at equivalence point, 5.00 ml, 5.01 ml, 10.00 ml

(ii) Plot the titration curve. (2)
(iii) Use the Henderson Equation to suggest a suitable indicator for the titration. (3)
(iv)Sketch the plot expected if 0.1000 M HCl above is replaced with 0.1000 M CH_3COOH, and state the difference between these two curves. (2)
(v) State the difference between "end point" and "equivalence" point in acid-base titrations (3)

Question 3 [25]

(a) In the technique of gravimetric analysis,

(i)State the Von Weimarn Ratio, and define all the terms in it. (3)
(ii)Using the Von Weimarn Ratio as reference, discuss the effects of relative supersaturation of a solution on the size of the crystalline precipitate formed in the solution concerned. (2)
(iii)What are the three ideal characteristics of a good analytical precipitate? (3)

(b) (i) Define "titration error" in precipitation titrations (2)
(ii) In precipitation titrations, $AgNO_3$, though not a primary standard, is universally used. What is meant by a "primary standard" (2)

(c) (i)Consider the titration of 50 ml of 0.0100M KBr with 0.025M $AgNO_3$, and calculate the pAg at the following volumes of $AgNO_3$ added: (5)

5 ml, 19 ml, 19.9 ml, 20 ml, 35 ml

(ii)Draw the titration curve for (i) above. (2)
(iii)On one graph, sketch three curves that you would expect to get for the system in (i) above for the following KBr concentrations:

0.005 M, 0.01 M, 0.015 M
clearly label each one. (3)

(iv) On one graph, sketch three curves that you would expect to get for the system in (i) above for the following salts:

0.01 M KBr, 0.01 M KCl, 0.01 M KI
Clearly label each one. (3)

Question 4 [25]

(a) In complexometric titrations,

(i) What does the acronym "EDTA" stand for, and draw its chemical structure (2)

(ii) Explain what is meant by the "Chelate Effect" (3)

(iii) Explain what is meant by an "Indirect Titration" (3)

(iv) Explain what is meant by a "Back Titration" (3)

(v) Draw the chemical structure of the indicator calmagite, and explain how it works in the titration of Mg^{2+} ions with EDTA (4)

(b) Calculate pFe given that log Kf for the $(EDTA)^-$ is 25.1 for a solution of 0.10M Fe $(EDTA)^-$ in pH=8 (3)

(c) Suppose a 25.00 ml solution of 0.02026 M Co^{2+} is titrated with 0.03855M EDTA at pH = 6.00. Calculate the pCo at the following volumes of EDTA added:

0.10 ml   12.00 ml   equivalence point volume   14.00 ml

and plot the titration curve. (5)

(d) Explain the role of an auxiliary complexing reagent in EDTA titrations. (2)

Question 5[25]

(a) (i) Use a chemical equation to state the difference between an oxidizing agent and a reducing agent. (2)

(i) Suppose that electrons are forced into a Pt wire immersed in a solution containing Sn^{4+}, which undergoes a two-electron change to Sn^{2+} at a constant rate of 4.24 mmol/hr. How much current in mA, flows into the solution? (5)

(b) An acid solution of $Na_2Cr_2O_7$ is mixed with a solution of KBr. A redox reaction occurs, resulting in Br_2 and Cr^{3+}. Write a balanced equation for the redox reaction. (3)

(c) For the redox system $Fe^{3+} + e^- \Leftrightarrow Fe^{2+}$, in which 0.58g of Fe^{3+}? Is starting material,

(i) How much charge should be applied to completely reduce the Fe^{3+}? (3)

(ii) If the process in (i) above were to take place in 10 minutes, how much constant current should be applied ($F=9.648 \times 10^4 C$)? (2)

(d) The standard hydrogen electrode (SHE) is the electrode against which all electrode potentials are referenced.

(i) Draw the SHE and label all its components. (3)

(ii) Write down the half cell reaction taking place in the SHE, and state the electrode potential.(2)

(iii) State the function of a salt bridge and explain how it works. (1)

(e) Suppose a 10 ml solution of 0.05 M Fe^{2+} is titrated with 0.100 M Ce^{4+} in 1 M $HClO_4$ and the potential measured relative to the saturated calomel electrode (SCE, E = 0.241V). Calculate the measured potential at the following values of 0.100 M Ce^{4+} added:

2.50 ml 4.99 ml 5.0 ml 7.00 ml

And plot the titration curve. (4)

Question 6[25]

(a) Ammonia, NH_3, is allowed to distribute between water at pH=5 and carbon tetrachloride, CCl_4.

(i) Write down the equilibrium equation in the aqueous phase (1)

(ii) Write down the distribution ratio expression for this solvent extraction system. (2)

(iii) Write down the distribution coefficient expression for this solvent extraction system (2)

(b) Describe four desirable properties of an ideal choice of solvent in liquid-liquid extraction (4)

(c) Extractions are enhanced through the use of chelation. Write down the chemical structures of the following chelating agents

(i) Oxime (2)

(ii) Dithizone (2)

(d) In the determination of trace nickel by liquid-liquid extraction, several reagents are added prior to the extraction step.

(i) Name and write chemical structure of the compound used to form the nickel complex that extracts into chloroform (3)

(ii) Explain the role of hydroxylamine hydrochloride in the analysis (2)

(iii) Explain the role of pH 6.5 acetate buffer in this analysis (2)

(e) The distribution ratio of iodine gas (at. Wt. = 126.9045) between water and carbon tetrachloride is 85. A 50-mL solution containing 0.35 grams of iodine and 75 ppm of Cd is mixed with 25 mL of carbon tetrachloride in order to remove the iodine into the organic phase. Calculate the number of times that the extraction needs to be performed in order to get 99.999% of the iodine into the organic phase. (5)

1. PERIODIC CHART OF THE ELEMENTS

1 1A	2 2A	3 3B	4 4B	5 5B	6 6B	7 7B	8	9 8B	10	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 132.9055	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.

★ 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 STABII CONSTANT

$Ag(CN)_2^-$	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.

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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

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

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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 ENERG

(All negative) kJ

	F	Cl	Br
Li	1030	840	781
Na	914	770	728
K	812	701	671
Rb	780	682	654
Cs	744	630	613

10. HALF LIVES

H^3	12.3 years	K^{40}	1.28×10^9y	I^{131}	8.1 d
F^{20}	11.4 secs	Ca^{45}	165 days	Cs^{137}	30 y
C^{14}	5730 years	Fe^{59}	45 days	Au^{198}	2.69
Na^{24}	15.0 hours	Co^{60}	5.26 y	Ra^{226}	1620
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}	24,4

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Electrode Potentials, $E^\ominus$

$H^+ + e^- \rightleftharpoons \frac{1}{2}H_2 \quad E^\ominus = 0.000V$

$Cd^{2+} + 2e \rightleftharpoons Cd(s) \quad E^\ominus = -0.246V$

$AgCl + e^- \rightleftharpoons Ag(s) + Cl^- \quad E^\ominus = -0.023V$

$Cu^{2+} + 2e^- \rightleftharpoons Cu(s) \quad E^\ominus =$

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

11. 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	MISC.		275	192

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}	$t_{9…}$
1	1.0	6.3	13
2	0.82	2.9	4.
3	0.76	2.35	3.
4	0.74	2.13	2.
5	0.73	2.02	2
6	0.72	1.94	2
7	0.71	1.90	2
8	0.71	1.86	2
9	0.70	1.83	2
10	0.70	1.81	2
20	0.69	1.72	2
30	0.68	1.70	2
∞	0.67	1.64	1

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

$Na^+ + e \rightleftarrows Na$	− 2.713
$Mg^{++} + 2e \rightleftarrows Mg$	− 2.37
$Al^{+++} + 3e \rightleftarrows Al$	− 1.66
$Zn^{++} + 2e \rightleftarrows Zn$	− 0.763
$Fe^{++} + 2e \rightleftarrows Fe$	− 0.44
$Cd^{++} + 2e \rightleftarrows Cd$	− 0.403
$Cr^{+++} + e \rightleftarrows Cr^{++}$	− 0.38
$Tl^+ + e \rightleftarrows Tl$	− 0.336
$V^{+++} + e \rightleftarrows V^{++}$	− 0.255
$Sn^{++} + 2e \rightleftarrows Sn$	− 0.14
$Pb^{++} + 2e \rightleftarrows Pb$	− 0.126
$2H^+ + 2e \rightleftarrows H_2$	0.000
$S_4O_6^= + 2e \rightleftarrows 2S_2O_3^=$	0.09
$TiO^{++} + 2H^+ + e \rightleftarrows Ti^{+++} + H_2O$	0.10
$S + 2H^+ + 2e \rightleftarrows H_2S$	0.14
$Sn^{+4} + 2e \rightleftarrows Sn^{++}$	0.14
$Cu^{++} + e \rightleftarrows Cu^+$	0.17
$SO_4^= + 4H^+ + 2e \rightleftarrows H_2O + H_2SO_3$	0.17
$AgCl + e \rightleftarrows Cl^- + Ag$	0.222
Saturated calomel	(0.244)
$Hg_2Cl_2 + 2e \rightleftarrows 2Cl^- + 2Hg$	0.268
$Bi^{+++} + 3e \rightleftarrows Bi$	0.293
$UO_2^{++} + 4H^+ + 2e \rightleftarrows U^{+4} + 2H_2O$	0.33
$VO^{++} + 2H^+ + e \rightleftarrows V^{+++} + H_2O$	0.34
$Cu^{++} + 2e \rightleftarrows Cu$	0.34
$Fe(CN)_6^{-3} + e \rightleftarrows Fe(CN)_6^{-4}$	0.355
$Cu^+ + e \rightleftarrows Cu$	0.52
$I_3^- + 2e \rightleftarrows 3I^-$	0.545
$H_3AsO_4 + 2H^+ + 2e \rightleftarrows H_3AsO_3 + H_2O$	0.56
$I_2 + 2e \rightleftarrows 2I^-$	0.621
$2HgCl_2 + 2e \rightleftarrows Hg_2Cl_2 + 2Cl^-$	0.63
$O_2 + 2H^+ + 2e \rightleftarrows H_2O_2$	0.69
Quinone + $2H^+ + 2e \rightleftarrows$ Hydroquinone	0.70
$Fe^{+++} + e \rightleftarrows Fe^{++}$	0.771
$Hg_2^{++} + 2e \rightleftarrows 2Hg$	0.792
$Ag^+ + e \rightleftarrows Ag$	0.799
$Hg^{++} + 2e \rightleftarrows Hg$	0.851
$2Hg^{++} + 2e \rightleftarrows Hg_2^{++}$	0.907
$NO_3^- + 3H^+ + 2e \rightleftarrows HNO_2 + H_2O$	0.94
$HNO_2 + H^+ + e \rightleftarrows NO + H_2O$	0.98
$VO_2^+ + 2H^+ + e \rightleftarrows VO^{++} + H_2O$	0.999
$Br_2 + 2e \rightleftarrows 2Br^-$	1.08
$2IO_3^- + 12H^+ + 10e \rightleftarrows 6H_2O + I_2$	1.19
$O_2 + 4H^+ + 4e \rightleftarrows 2H_2O$	1.229
$MnO_2 + 4H^+ + 2e \rightleftarrows Mn^{++} + 2H_2O$	1.23
$Cr_2O_7^= + 14H^+ + 6e \rightleftarrows 7H_2O + 2Cr^{+++}$	1.33
$Cl_2 + 2e \rightleftarrows 2Cl^-$	1.358
$2BrO_3^- + 12H^+ + 10e \rightleftarrows 6H_2O + Br_2$	1.50
$MnO_4^- + 8H^+ + 5e \rightleftarrows 4H_2O + Mn^{++}$	1.51
$Ce^{+4} + e \rightleftarrows Ce^{+3}$	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
1.0	0.606	0.20	0.045

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
C_{gra}	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. ΔG° 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	Wt…
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 c…

Water at		Air (70 cm…
0°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. = $\sqrt{\Sigma (X_i - \bar{X})^2/(\ldots}$
Conf. limits = $\bar{X} \pm ts/\sqrt{n}$
$E = E° - (0.0592/n)\log([Red]/\ldots$
$\log I_0/I_t = abc = A = \log 1/\ldots$
$\log N_T = \log N_0 - 0.301T/T_{\frac{1}{2}}$
$x = (-b \pm \sqrt{b^2 - 4ac})/2a$
$n\lambda = 2d \sin\theta$
$2.303 \log_{10} a = \log_e a$
$h = 6.626 \times 10^{-34}$ 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 = 1.661×10^{-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}
O °C = 273.15 K
1 eV = 1.602×10^{-19} J
1 cal = 4.1840 J

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.

Values of $\alpha_{Y^{4-}}$ for EDTA at 20 °C and μ = 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 (μ = 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, μ = 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 (μ = 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 (μ = 1.0)	Np^{4+}	24.6 (25 °C, μ = 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.