

**DEPARTMENT OF CHEMISTRY****UNIVERSITY OF SWAZILAND****C204****INTRODUCTION TO ANALYTICAL CHEMISTRY****MAY 2012 FINAL EXAMINATION****Time Allowed:****Three (3) Hours**

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**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. (i) Write down the equation that describes the Gaussian curve in chemometrics, and explain all terms appearing in it. (3)

(ii) A new gravimetric method is developed for Iron (III), in which the iron is precipitated in crystalline form with an organoboron cage compound. The accuracy of the method is checked by analysing the iron in an ore sample and comparing the results obtained using standard precipitation with ammonia and weighing of  $\text{Fe}_2\text{O}_3$ . The results, reported as % Fe for each analysis, were as follows;

<u>Test Method (%)</u>	<u>Reference Method (%)</u>
20.10	18.89
20.50	19.20
18.65	19.00
19.25	19.70
19.40	19.40
19.99	

Is there a significant difference between the two methods at the 95% confidence interval? (5)

(iii) In the gravimetric and reference methods of question (v) above, comment on the precisions at the 95% confidence level. (4)

- b. The following data was obtained from an analysis.

124            125            126            128            147

Should the value "147" be considered as part of the data at the 90% confidence interval? (3)

- c. (i) A 0.1000M solution of NaOH is used to titrate 10.00ml of 0.100M  $\text{CH}_3\text{COOH}$ . Calculate the pH at the following volumes of NaOH added during that titration (6)

1.00ml,

at equivalence point,

at 3ml past equivalence point

(ii) Plot the titration curve. (2)

(iii) Sketch the plot expected if a diprotic weak acid (e.g., oxalic acid) replaced  $\text{CH}_3\text{COOH}$  in the titration in (i) above. (2)

**Question 2 [25]**

- a. (i) Use an example to describe the mechanism of adsorption in gravimetric analysis. How can adsorption be minimized? (3)

(ii) Using  $\text{Ba}^{2+}$  as an example, describe what is meant by "occlusion" in gravimetry. How can occlusion be minimized? (3)

(iii) What is meant by "Ostwald Ripening" in gravimetric analysis, and how is it accomplished? (3)

- b. Consider the titration of 25mL of 0.100M KCl with 0.050M  $\text{AgNO}_3$  using the Mohr method, given the following:  $K_{sp} = \text{AgI}: 8.3 \times 10^{-17}$ ,  $\text{AgBr}: 5.0 \times 10^{-13}$ ,  $\text{AgCl}: 1.8 \times 10^{-10}$

(i) Name the indicator used for the Mohr method. (1)

(ii) Use equations to explain how the end point is detected using this indicator. (3)

(iii) Calculate the pAg at the following stages of titration: (6)

5mL added,                      at equivalence point,                      5mL past equivalence point

(iv) Plot the titration curve. (2)

- c. (i) Explain how pH affects the Mohr titration, and state how such effects are avoided. (2)  
 (ii) Explain how the indicator concentration affects the Mohr titration, and state how such effects are avoided. (2)

### **Question 3 [25]**

- a. For  $\text{CH}_3\text{NH}_2$ , as a non-aqueous solvent, write down the:  
 (i) Autoprotolysis equation. (1)  
 (ii) Expression for the equilibrium constant for autoprotolysis. (2)  
 (iii) Calculate the pH of a "neutral" solution, given that the autoprotolysis constant is  $3 \times 10^{-20}$ . (3)
- b. (i) Calculate the pH of a 400-mL buffer solution containing 0.200M  $\text{NH}_3$  and 0.300M  $\text{NH}_4\text{Cl}$ . (4)  
 (ii) Calculate the weight of  $\text{NH}_4\text{Cl}$  required to make this buffer. (3)  
 (iii) Commercial ammonia solution is 70%  $\text{NH}_3$  vol/vol, and density 0.85g/mL. What volume of commercial  $\text{NH}_3$  in mL, is required to make this buffer? (4)  
 (iv) Calculate the change in pH of the buffer system in 4(i) above upon addition of 10mL of 0.05M HCl. (2)  
 (v) Calculate the change in pH of the buffer system in 4(i) above upon addition of 10mL of 0.05M  $\text{Ba}(\text{OH})_2$  (2)
- c. (i) Give two (2) reasons why solvent extraction is carried out in analytical chemistry. (2)  
 (ii) State the "Distribution Law" of solvent extraction, and express it mathematically. (2)

### **Question 4 [25]**

- a. (i) Use an example to describe the "chelate effect". (2)  
 (ii) State two (2) elements that are best extracted into ether after forming metal-chloro complexes. (2)  
 (iii) Name and draw the chemical structure of a commonly used chelation agent for  $\text{Al}^{3+}$ . (1)  
 (iv) Name and draw the chemical structure of a commonly used chelation agent for  $\text{Ni}^{2+}$ . (1)
- b. (i) Draw the chemical structure of EDTA, and write down the expression relating the fraction dissociated to the formation constant and pH. (4)  
 (ii) What is meant by conditional formation constant in EDTA titrations? (2)
- c. Consider the titration of 50mL 0.05M  $\text{Mg}^{2+}$  in a pH = 10.00 buffer with 0.05M EDTA as titrant. Calculate the pMg at the following volumes of EDTA added: (8)
- 0mL                      5mL                      50mL                      51mL
- d. (i) Draw the chemical structure of the indicator Eriochrome Black T. (2)  
 (ii) Use equations to explain how the indicator Eriochrome Black T works in EDTA titrations. (3)

**Question 5 [25]**

- a. (i) What is the difference between “Galvanic” and “non-Galvanic” electrochemical cells? (2)  
 (ii) Consider the cell reaction  $\text{Cu(s)} + \text{PbF}_2\text{(s)} \rightleftharpoons \text{Cu}^{2+} + 2\text{F}^- + \text{Pb(s)}$  and indicate whether it would be Galvanic as written. (4)
- b. (i) Draw and label the silver-silver chloride reference electrode. (4)  
 (ii) Write down the half cell reaction taking place inside the electrode in b(i) above, and state its potential. (2)
- c. A titration is carried out in a cell, whereby the potential vs SCE (0.241V) is measured for a 25ml solution of 0.020M  $\text{Cr}^{2+}$  ( $E^0 = -0.41\text{V}$ ) titrated with 0.010M  $\text{Fe}^{3+}$  ( $E^0 = 0.770\text{V}$ ).
- (i) Calculate the potential (vs SCE) after addition of the following volumes during the titration: (6)
- |        |         |       |
|--------|---------|-------|
| 5.00ml | 50.00ml | 100ml |
|--------|---------|-------|
- (ii) Sketch the titration curve. (2)  
 (iii) Use chemical equations to explain how redox indicators are chosen in electrochemical titrations. (3)
- d. Use chemical equations to explain the technique of iodimetry in redox chemistry. (2)

**Question 6 [25]**

- a. (i) Describe the principle of “indirect titration” in analytical chemistry. (3)  
 (ii) Suppose an unknown is  $\text{Cl}^-$  ion in 25mL of a water sample, and that 30mL of 0.01M  $\text{AgNO}_3$  was added to it, and that a titration of the resulting solution with 0.01M  $\text{HCl}$  took 5mL, calculate the concentration of  $\text{Cl}^-$  in the sample. (5)  
 (iv) In the Volhard method of indirect titration, explain how the indicator works. (3)  
 (v) What is the main disadvantage of the Volhard method, and describe the two ways on which this can be overcome. (3)
- b. Use chemical equations to explain how the Karl Fischer Method for the determination of water works. (4)
- c. (i) Explain why  $\text{I}_2$  is an excellent primary standard, but still needs standardization. Name the commonly used reagent for this purpose. (3)  
 (ii)  $\text{Na}_2\text{S}_2\text{O}_3$  is widely used as a titrant for the iodimetric determination of Cu. Use equations to describe how  $\text{Na}_2\text{S}_2\text{O}_3$  is standardized in these titrations. (4)

## SOME STANDARD AND FORMAL ELECTRODE POTENTIALS

Half-reaction*	$E^\circ, V$	Formal potential, V
$Ag^+ + e \rightleftharpoons Ag(s)$	+0.799	0.228, 1 M HCl; 0.792, 1 M HClO <sub>4</sub> ; 0.77, 1 M H <sub>2</sub> SO <sub>4</sub>
$AgBr(s) + e \rightleftharpoons Ag(s) + Br^-$	+0.073	
$AgCl(s) + e \rightleftharpoons Ag(s) + Cl^-$	+0.222	0.228, 1 M KCl
$Ag(CN)_2^- + e \rightleftharpoons Ag(s) + 2CN^-$	-0.31	
$Ag_2CrO_4(s) + 2e \rightleftharpoons 2Ag(s) + CrO_4^{2-}$	+0.446	
$AgI(s) + e \rightleftharpoons Ag(s) + I^-$	-0.151	
$Ag(S_2O_3)_3^{4-} + e \rightleftharpoons Ag(s) + 2S_2O_3^{2-}$	+0.017	
$Al^{3+} + 3e \rightleftharpoons Al(s)$	-1.662	
$H_3AsO_4 + 2H^+ + 2e \rightleftharpoons H_3AsO_3 + H_2O$	+0.559	0.577, 1 M HCl, HClO <sub>4</sub>
$Ba^{2+} + 2e \rightleftharpoons Ba(s)$	-2.906	
$BiO^+ + 2H^+ + 3e \rightleftharpoons Bi(s) + H_2O$	+0.320	
$BiCl_4^- + 3e \rightleftharpoons Bi(s) + 4Cl^-$	+0.16	
$Br_2(l) + 2e \rightleftharpoons 2Br^-$	+1.065	1.05, 4 M HCl
$Br_2(aq) + 2e \rightleftharpoons 2Br^-$	+1.0871	
$BrO_3^- + 6H^+ + 5e \rightleftharpoons \frac{1}{2}Br_2(l) + 3H_2O$	+1.52	
$BrO_3^- + 6H^+ + 6e \rightleftharpoons Br^- + 3H_2O$	+1.44	
$Cu^{2+} + 2e \rightleftharpoons Cu(s)$	-2.866	
$C_6H_4O_2$ (quinone) + 2H <sup>+</sup> + 2e $\rightleftharpoons$ C <sub>6</sub> H <sub>4</sub> (OH) <sub>2</sub>	+0.699	0.696, 1 M HCl, HClO <sub>4</sub> , H <sub>2</sub> SO <sub>4</sub>
$2CO_2(g) + 2H^+ + 2e \rightleftharpoons H_2C_2O_4$	-0.49	
$Cd^{2+} + 2e \rightleftharpoons Cd(s)$	-0.403	
$Ce^{4+} + e \rightleftharpoons Ce^{3+}$		1.70, 1 M HClO <sub>4</sub> ; 1.61, 1 M HNO <sub>3</sub> ; 1.44, 1 M H <sub>2</sub> SO <sub>4</sub> ; 1.28, 1 M HCl
$Cl_2(g) + 2e \rightleftharpoons 2Cl^-$	+1.359	
$HClO + H^+ + e \rightleftharpoons \frac{1}{2}Cl_2(g) + H_2O$	+1.63	
$ClO_2^- + 6H^+ + 5e \rightleftharpoons \frac{1}{2}Cl_2(g) + 3H_2O$	+1.47	
$Co^{2+} + 2e \rightleftharpoons Co(s)$	-0.277	
$Co^{3+} + e \rightleftharpoons Co^{2+}$	+1.808	
$Cr^{3+} + e \rightleftharpoons Cr^{2+}$	-0.408	
$Cr^{3+} + 3e \rightleftharpoons Cr(s)$	-0.744	
$Cr_2O_7^{2-} + 14H^+ + 6e \rightleftharpoons 2Cr^{3+} + 7H_2O$	+1.33	
$Cu^{2+} + 2e \rightleftharpoons Cu(s)$	+0.337	
$Cu^{2+} + e \rightleftharpoons Cu^+$	+0.153	
$Cu^+ + e \rightleftharpoons Cu(s)$	+0.521	
$Cu^{2+} + I^- + e \rightleftharpoons CuI(s)$	+0.86	
$CuI(s) + e \rightleftharpoons Cu(s) + I^-$	-0.185	
$F_2(g) + 2H^+ + 2e \rightleftharpoons 2HF(aq)$	+3.06	
$Fe^{2+} + 2e \rightleftharpoons Fe(s)$	-0.440	
$Fe^{3+} + e \rightleftharpoons Fe^{2+}$	+0.771	0.700, 1 M HCl; 0.732, 1 M HClO <sub>4</sub> ; 0.68, 1 M H <sub>2</sub> SO <sub>4</sub> ; 0.71, 1 M HCl; 0.72, 1 M HClO <sub>4</sub> , H <sub>2</sub> SO <sub>4</sub>
$Fe(CN)_6^{3-} + e \rightleftharpoons Fe(CN)_6^{4-}$	+0.36	-0.005, 1 M HCl, HClO <sub>4</sub> ; 0.274, 1 M HCl; 0.776, 1 M HClO <sub>4</sub> ; 0.674, 1 M H <sub>2</sub> SO <sub>4</sub> ; 0.907, 1 M HClO <sub>4</sub>
$2H^+ + 2e \rightleftharpoons H_2(g)$	0.000	
$Hg_2^{2+} + 2e \rightleftharpoons 2Hg(l)$	+0.788	
$2Hg^{2+} + 2e \rightleftharpoons Hg_2^{2+}$	+0.920	
$Hg^{2+} + 2e \rightleftharpoons Hg(l)$	+0.854	
$Hg_2Cl_2(s) + 2e \rightleftharpoons 2Hg(l) + 2Cl^-$	+0.268	0.242, sat'd KCl; 0.282, 1 M KCl; 0.334, 0.1 M KCl
$Hg_2SO_4(s) + 2e \rightleftharpoons 2Hg(l) + SO_4^{2-}$	+0.615	
$HO_2^- + H_2O + 2e \rightleftharpoons 3OH^-$	+0.88	

(CONTINUED)  
SOME STANDARD AND FORMAL ELECTRODE POTENTIALS

Half-reaction*	$E^\circ$ , V	Formal potential, V
$I_2(s) + 2e \rightleftharpoons 2I^-$	+0.5355	
$I_2(aq) + 2e \rightleftharpoons 2I^-$	+0.6151	
$I_3^- + 2e \rightleftharpoons 3I^-$	+0.536	
$ICl_2^- + e \rightleftharpoons \frac{1}{2}I_2(s) + 2Cl^-$	+1.056	
$IO_3^- + 6H^+ + 5e \rightleftharpoons \frac{1}{2}I_2(s) + 3H_2O$	+1.196	
$IO_3^- + 6H^+ + 5e \rightleftharpoons \frac{1}{2}I_2(aq) + 3H_2O$	+1.178†	
$IO_3^- + 2Cl^- + 6H^+ + 4e \rightleftharpoons ICl_2^- + 3H_2O$	+1.24	
$H_2IO_4 + H^+ + 2e \rightleftharpoons IO_3^- + 3H_2O$	+1.601	
$K^+ + e \rightleftharpoons K(s)$	-2.925	
$Li^+ + e \rightleftharpoons Li(s)$	-3.045	
$Mg^{2+} + 2e \rightleftharpoons Mg(s)$	-2.363	
$Mn^{2+} + 2e \rightleftharpoons Mn(s)$	-1.180	
$Mn^{2+} + e \rightleftharpoons Mn^{3+}$		1.51, 7.5 M $H_2SO_4$
$MnO_2(s) + 4H^+ + 2e \rightleftharpoons Mn^{2+} + 2H_2O$	+1.23	1.24, 1 M $HClO_4$
$MnO_4^- + 8H^+ + 5e \rightleftharpoons Mn^{2+} + 4H_2O$	+1.51	
$MnO_4^- + 4H^+ + 3e \rightleftharpoons MnO_2(s) + 2H_2O$	+1.695	
$MnO_4^- + e \rightleftharpoons MnO_4^{2-}$	+0.564	
$N_2(g) + 5H^+ + 4e \rightleftharpoons N_2H_5^+$	-0.23	
$HNO_2 + H^+ + e \rightleftharpoons NO(g) + H_2O$	+1.00	
$NO_3^- + 3H^+ + 2e \rightleftharpoons HNO_2 + H_2O$	+0.94	0.92, 1 M $HNO_3$
$Na^+ + e \rightleftharpoons Na(s)$	-2.714	
$Ni^{2+} + 2e \rightleftharpoons Ni(s)$	-0.250	
$H_2O_2 + 2H^+ + 2e \rightleftharpoons 2H_2O$	+1.776	
$O_2(g) + 4H^+ + 4e \rightleftharpoons 2H_2O$	+1.229	
$O_2(g) + 2H^+ + 2e \rightleftharpoons H_2O_2$	+0.682	
$O_2(g) + 2H^+ + 2e \rightleftharpoons O_2(g) + H_2O$	+2.07	
$Pb^{2+} + 2e \rightleftharpoons Pb(s)$	-0.126	-0.14, 1 M $HClO_4$ ; -0.29, 1 M $H_2SO_4$
$PbO_2(s) + 4H^+ + 2e \rightleftharpoons Pb^{2+} + 2H_2O$	+1.455	
$PbSO_4(s) + 2e \rightleftharpoons Pb(s) + SO_4^{2-}$	-0.350	
$PtCl_6^{2-} + 2e \rightleftharpoons Pt(s) + 4Cl^-$	+0.73	
$PtCl_4^{2-} + 2e \rightleftharpoons PtCl_2(s) + 2Cl^-$	+0.68	
$Pd^{2+} + 2e \rightleftharpoons Pd(s)$	+0.987	
$S(s) + 2H^+ + 2e \rightleftharpoons H_2S(g)$	+0.141	
$H_2SO_3 + 4H^+ + 4e \rightleftharpoons S(s) + 3H_2O$	+0.450	
$S_2O_8^{2-} + 2e \rightleftharpoons 2S_2O_4^{2-}$	+0.08	
$SO_4^{2-} + 4H^+ + 2e \rightleftharpoons H_2SO_3 + H_2O$	+0.172	
$S_2O_8^{2-} + 2e \rightleftharpoons 2SO_4^{2-}$	+2.01	
$Sb_2O_3(s) + 6H^+ + 4e \rightleftharpoons 2SbO^+ + 3H_2O$	+0.581	
$H_2SeO_3 + 4H^+ + 4e \rightleftharpoons Se(s) + 3H_2O$	+0.740	
$SeO_4^{2-} + 4H^+ + 2e \rightleftharpoons H_2SeO_3 + H_2O$	+1.15	
$Sn^{2+} + 2e \rightleftharpoons Sn(s)$	-0.136	-0.16, 1 M $HClO_4$
$Sn^{4+} + 2e \rightleftharpoons Sn^{2+}$	+0.154	0.17, 1 M $HCl$
$Ti^{3+} + e \rightleftharpoons Ti^{2+}$	-0.369	
$TiO^{2+} + 2H^+ + e \rightleftharpoons Ti^{2+} + H_2O$	+0.099	0.04, 1 M $H_2SO_4$
$Tl^+ + e \rightleftharpoons Tl(s)$	-0.336	-0.551, 1 M $HCl$ ; -0.33, 1 M $HClO_4$ , $H_2SO_4$
$Tl^{2+} + 2e \rightleftharpoons Tl^+$	+1.25	0.77, 1 M $HCl$
$UO_2^{2+} + 4H^+ + 2e \rightleftharpoons U^{4+} + 2H_2O$	+0.334	
$V^{3+} + e \rightleftharpoons V^{2+}$	-0.256	-0.21, 1 M $HClO_4$
$VO^{2+} + 2H^+ + e \rightleftharpoons V^{3+} + H_2O$	+0.359	
$V(OH)_4^+ + 2H^+ + e \rightleftharpoons VO^{2+} + 3H_2O$	+1.00	1.02, 1 M $HCl$ , $HClO_4$
$Zn^{2+} + 2e \rightleftharpoons Zn(s)$	-0.763	

\* Sources for  $E^\circ$  values: A. J. deBethune and N. A. S. Laund, *Standard Aqueous Electrode Potentials and Temperature Coefficients at 25°C*. Skokie, Ill.: Clifford A. Hampel, 1964, and G. Milazzo, S. Caroli, and V. K. Sharma, *Tables of Standard Electrode Potentials*. New York: Wiley, 1978. Source of formal potentials: E. H. Swift and E. A. Butler, *Quantitative Measurements and Chemical Equilibria*. San Francisco: W. H. Freeman and Company. Copyright © 1972.

† These potentials are hypothetical because they correspond to solutions that are 1.00 M in  $Br_2$  or  $I_2$ . The solubilities of these two compounds at 25°C are 0.18 M and 0.0020 M, respectively. In saturated solutions containing an excess of  $Br_2(l)$  or  $I_2(s)$ , the standard potentials for the half-reactions  $Br_2(l) + 2e \rightleftharpoons 2Br^-$  or  $I_2(s) + 2e \rightleftharpoons 2I^-$  should be used. On the other hand, at  $Br_2$  and  $I_2$  concentrations less than saturation, these hypothetical electrode potentials should be employed.



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

$v_2$	$v_1$					
	2	3	4	5	6	$\infty$
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
$\infty$	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 (" $\alpha$ )				
	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
$\infty$	0.674	1.282	1.645	1.960	2.576

Table 4-4 Values of  $Q$  for rejection of data

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



1. PERIODIC CHART OF THE ELEMENTS

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

★ Lanthanide series  
▲ Actinide series

4. NET STABILITY CONSTANTS

Ag(CN) <sub>2</sub> <sup>-</sup>	5 × 10 <sup>21</sup>
Ag(NH <sub>3</sub> ) <sub>2</sub> <sup>+</sup>	1.6 × 10 <sup>7</sup>
Ag(S <sub>2</sub> O <sub>3</sub> ) <sub>2</sub> <sup>-3</sup>	4.7 × 10 <sup>13</sup>
Al(OH) <sub>4</sub> <sup>-</sup>	1.0 × 10 <sup>33</sup>
Ca(EDTA)	1.0 × 10 <sup>10</sup>
Cd(CN) <sub>4</sub>	8.3 × 10 <sup>16</sup>
Cd(NH <sub>3</sub> ) <sub>4</sub> <sup>++</sup>	5.5 × 10 <sup>5</sup>
Co(NH <sub>3</sub> ) <sub>6</sub> <sup>+3</sup>	2 × 10 <sup>4</sup>
Cr(OH) <sub>4</sub> <sup>-</sup>	4 × 10 <sup>3</sup>
Cu(CN) <sub>4</sub> <sup>-3</sup>	1 × 10 <sup>25</sup>
Cu(NH <sub>3</sub> ) <sub>4</sub> <sup>++</sup>	1.2 × 10 <sup>4</sup>
Fe(CN) <sub>6</sub> <sup>-3</sup>	4.0 × 10 <sup>16</sup>
Fe(CN) <sub>6</sub> <sup>-4</sup>	2.5 × 10 <sup>35</sup>
Fe(SCN) <sub>2</sub> <sup>++</sup>	1.0 × 10 <sup>3</sup>
HgCl <sub>4</sub>	1.3 × 10 <sup>16</sup>
Hg(CN) <sub>4</sub>	8.3 × 10 <sup>16</sup>
Hg(SCN) <sub>4</sub>	5.0 × 10 <sup>16</sup>
HgI <sub>4</sub>	6.3 × 10 <sup>16</sup>
Mg(EDTA)	1.3 × 10 <sup>8</sup>
Ni(NH <sub>3</sub> ) <sub>6</sub> <sup>++</sup>	4.7 × 10 <sup>8</sup>
Pb(OH) <sub>3</sub> <sup>-</sup>	7.9 × 10 <sup>14</sup>
Zn(CN) <sub>4</sub>	4.2 × 10 <sup>16</sup>
Zn(NH <sub>3</sub> ) <sub>4</sub> <sup>++</sup>	7.8 × 10 <sup>8</sup>
Zn(OH) <sub>4</sub>	6.3 × 10 <sup>16</sup>

2. IONIZATION CONSTANTS (K<sub>a</sub>) FOR WEAK ACIDS

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

3. SOLUBILITY PRODUCT CONSTANTS

AgBr	4 × 10 <sup>-13</sup>	BaC <sub>2</sub> O <sub>4</sub>	2 × 10 <sup>-8</sup>	KClO <sub>4</sub>	2 × 10 <sup>-2</sup>
Ag <sub>2</sub> CO <sub>3</sub>	6 × 10 <sup>-12</sup>	BaSO <sub>4</sub>	1 × 10 <sup>-10</sup>	MgCO <sub>3</sub>	1 × 10 <sup>-5</sup>
AgCl	1 × 10 <sup>-10</sup>	CaCO <sub>3</sub>	5 × 10 <sup>-9</sup>	MgC <sub>2</sub> O <sub>4</sub>	9 × 10 <sup>-5</sup>
Ag <sub>2</sub> CrO <sub>4</sub>	2 × 10 <sup>-12</sup>	CaF <sub>2</sub>	4 × 10 <sup>-11</sup>	MgNH <sub>4</sub> PO <sub>4</sub>	2 × 10 <sup>-13</sup>
Ag[Ag(CN) <sub>2</sub> ] <sub>4</sub>	4 × 10 <sup>-12</sup>	CaC <sub>2</sub> O <sub>4</sub>	2 × 10 <sup>-9</sup>	Mg(OH) <sub>2</sub>	1 × 10 <sup>-11</sup>
AgI	1 × 10 <sup>-16</sup>	CdS	1 × 10 <sup>-28</sup>	MnS	1 × 10 <sup>-15</sup>
Ag <sub>3</sub> PO <sub>4</sub>	1 × 10 <sup>-19</sup>	Cu(OH) <sub>2</sub>	2 × 10 <sup>-20</sup>	PbCrO <sub>4</sub>	2 × 10 <sup>-14</sup>
Ag <sub>2</sub> S	1 × 10 <sup>-50</sup>	CuS	1 × 10 <sup>-36</sup>	PbS	1 × 10 <sup>-28</sup>
Ag <sub>2</sub> CNS	1 × 10 <sup>-12</sup>	Fe(OH) <sub>3</sub>	1 × 10 <sup>-36</sup>	PbSO <sub>4</sub>	2 × 10 <sup>-8</sup>
Al(OH) <sub>3</sub>	2 × 10 <sup>-32</sup>	Hg <sub>2</sub> Br <sub>2</sub>	3 × 10 <sup>-23</sup>	SrCrO <sub>4</sub>	4 × 10 <sup>-5</sup>
BaCO <sub>3</sub>	5 × 10 <sup>-9</sup>	Hg <sub>2</sub> Cl <sub>2</sub>	6 × 10 <sup>-19</sup>	Zn(OH) <sub>2</sub>	3.6 × 10 <sup>-16</sup>
BaCrO <sub>4</sub>	1 × 10 <sup>-10</sup>	Hg <sub>2</sub> S	1 × 10 <sup>-52</sup>	ZnS	1 × 10 <sup>-24</sup>

5. FIRST IONIZATION ENERGIES, e.v.

1A	2A											14											18	19	20	21	22
5.4	9.3																						6.0	8.1	11	13	12
5.1	7.6	38	48	58	68	78						18	28	38	48	58	68	78	88	98							
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	12											
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	10											
3.9	5.2	5.9	6.3	6	6.0	7.9	8.7	9.2	9.0	9.2	10	6.1	7.4	8													

6. ELECTRONEGATIVITIES, Pauling

1A	2A											14											18	19	20	21	22
1.0	1.5																						1.5	1.8	2.1	2.3	3.0
0.9	1.2	38	48	58	68	78						18	28	38	48	58	68	78	88	98							
0.8	1.0	1.3	1.5	1.6	1.6	1.8	1.8	1.8	1.8	1.9	1.6	1.8	1.8	2.0	2.4	2.8											
0.8	1.0	1.3	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	2.8											
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	2.2											

7. ATOMIC RADII picometers

1A	2A											14											18	19	20	21	22
153	112																						98	91	92	73	71
190	160	38	48	58	68	78						18	28	38	48	58	68	78	88	98							
235	197	182	147	134	130	135	128	125	124	128	138	141	137	139	140	114											
248	215	178	160	148	138	135	134	134	137	144	154	166	162	169	160	123											
267	222	187	167	148	141	137	135	136	139	146	157	171	175	170	176												

8. IONIC RADII pm

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

9. LATTICE ENERGIES (All negative) kJ/mol

Li	1030	840	781	7
Na	914	770	728	6
K	812	701	671	6
Rb	780	682	654	6
Cs	744	630	613	6

10. HALF LIVES

H <sup>3</sup>	12.3 years	K <sup>40</sup>	1.28 × 10 <sup>9</sup> y	I <sup>131</sup>	8.1 day
F <sup>20</sup>	11.4 secs	Ca <sup>45</sup>	165 days	Cs <sup>137</sup>	30 yes
C <sup>14</sup>	5730 years	Fe <sup>59</sup>	45 days	Au <sup>198</sup>	2.69 da
Na <sup>24</sup>	15.0 hours	Co <sup>60</sup>	5.26 y	Ra <sup>226</sup>	1620 y
P <sup>32</sup>	14.3 days	Br <sup>82</sup>	35.5 hours	U <sup>235</sup>	7.1 × 10 <sup>8</sup> y
S <sup>35</sup>	88 days	Sr <sup>90</sup>	28 years	U <sup>238</sup>	4.51 × 10 <sup>9</sup> y
Cl <sup>36</sup>	3.1 × 10 <sup>5</sup> y	I <sup>129</sup>	1.7 × 10 <sup>7</sup> y	Pu <sup>239</sup>	24,400 y

Electrode Potentials, E<sup>0</sup>

H<sup>+</sup> + e<sup>-</sup> ⇌ 1/2 H<sub>2</sub> E<sup>0</sup> = 0.000 V

Ca<sup>2+</sup> + 2e<sup>-</sup> ⇌ Ca(s) E<sup>0</sup> = -0.246 V

Cu<sup>2+</sup> + 2e<sup>-</sup> ⇌ Cu(s) E<sup>0</sup> = +0.34 V

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

pH	$\alpha_{Y^{4-}}$
0	$1.3 \times 10^{-23}$
1	$1.9 \times 10^{-18}$
2	$3.3 \times 10^{-14}$
3	$2.6 \times 10^{-11}$
4	$3.8 \times 10^{-9}$
5	$3.7 \times 10^{-7}$
6	$2.3 \times 10^{-5}$
7	$5.0 \times 10^{-4}$
8	$5.6 \times 10^{-3}$
9	$5.4 \times 10^{-2}$
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 <sup>+</sup>	2.79	Mn <sup>2+</sup>	25.3 (25°C)	Ce <sup>3+</sup>	15.98
Na <sup>+</sup>	1.66	Fe <sup>2+</sup>	25.1	Pb <sup>2+</sup>	16.40
K <sup>+</sup>	0.8	Co <sup>2+</sup>	41.4 (25°C)	Nd <sup>3+</sup>	16.61
Be <sup>2+</sup>	9.2	Zn <sup>2+</sup>	29.5	Pm <sup>3+</sup>	17.0
Mg <sup>2+</sup>	8.79	Hf <sup>4+</sup>	29.5 ( $\mu = 0.2$ )	Sm <sup>3+</sup>	17.14
Ca <sup>2+</sup>	10.69	VO <sup>2+</sup>	18.8	Eu <sup>3+</sup>	17.35
Sr <sup>2+</sup>	8.73	VO <sup>3+</sup>	15.55	Gd <sup>3+</sup>	17.37
Ba <sup>2+</sup>	7.86	Ag <sup>+</sup>	7.32	Tb <sup>3+</sup>	17.93
Ra <sup>2+</sup>	7.1	Tl <sup>+</sup>	6.54	Dy <sup>3+</sup>	18.30
Sc <sup>3+</sup>	23.1	Pd <sup>2+</sup>	18.5 (25°C)	Ho <sup>3+</sup>	18.62
			$\mu = 0.2$		
Y <sup>3+</sup>	18.09			Er <sup>3+</sup>	18.85
La <sup>3+</sup>	15.50			Tm <sup>3+</sup>	19.32
V <sup>3+</sup>	12.7	Zn <sup>2+</sup>	16.50	Yb <sup>3+</sup>	19.51
Cd <sup>2+</sup>	13.6	Cd <sup>2+</sup>	16.46	Lu <sup>3+</sup>	19.83
Mn <sup>2+</sup>	13.87	Hg <sup>2+</sup>	21.7	Am <sup>3+</sup>	17.8 (25°C)
Fe <sup>2+</sup>	14.32	Sn <sup>2+</sup>	18.3 ( $\mu = 0$ )	Cm <sup>3+</sup>	18.1 (25°C)
Co <sup>2+</sup>	16.31	Pb <sup>2+</sup>	18.04	Bk <sup>3+</sup>	18.5 (25°C)
Ni <sup>2+</sup>	18.62	Al <sup>3+</sup>	16.3	Cf <sup>3+</sup>	18.7 (25°C)
Cu <sup>2+</sup>	18.80	Ga <sup>3+</sup>	20.3		
Ti <sup>3+</sup>	21.3 (25°C)	In <sup>3+</sup>	25.0	Th <sup>4+</sup>	23.2
V <sup>5+</sup>	26.0	Tl <sup>3+</sup>	37.8 ( $\mu = 1.0$ )	U <sup>4+</sup>	25.8
Ce <sup>4+</sup>	23.4	Bj <sup>3+</sup>	27.8	Np <sup>4+</sup>	24.6 (25°C; $\mu = 1.0$ )

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. F. Martell and R. M. Smith, *Critical Stability Constants*, Vol. 1 (New York: Plenum Press, 1974), pp. 204-211.