

**DEPARTMENT OF CHEMISTRY  
UNIVERSITY OF SWAZILAND**

C304

**INSTRUMENTAL ANALYSIS**

**JULY 2006 SUPPLEMENTARY EXAMINATION**

**Time Allowed: Three (3) Hours**

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**Instructions:**

1. This examination has six (6) questions and one data sheet. The total number of pages is eight (8) 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.

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

## SECTION A      SPECTROSCOPY

Answer any two (2) questions from this section

### Question 1 [25]

- a) For a spectroscopic band occurring at  $1685 \text{ cm}^{-1}$ ,
- (i) convert to energy in joules [1]
  - (ii) state in which region of the electromagnetic spectrum the band falls [1]
  - (iii) state the kind of transition taking place [1]
- b) Explain using diagrams, why atomic spectra appear as lines, whereas molecular spectra appear as bands [4]
- c) The cheapest (affordable) uv-visible instruments (typically the *Bosch and Laumb Spectronic 20* series) rely on the use of a “Bunsen” arrangement of the optical components.
- (i) By means of a diagram, explain what is meant by this arrangement. [3]
  - (ii) Explain how this arrangement enables light from the source to be split into individual wavelengths. [3]
- d) The cheapest (affordable) infrared instruments rely on the use of a “Czerny-Turner” arrangement of the optical components.
- (i) By means of a diagram, explain what is meant by this arrangement. [3]
  - (ii) Explain how this arrangement enables light from the source to be split into individual wavelengths. [3]
- e) In the *Jasco* instrument used by researchers at the University of Swaziland for functional group identification of molluscicidal compounds in traditional herbs, a bolometer is used for detection. With the aid of a diagram, explain how this component works. [4]
- f) State two (2) reasons why in the *Jasco* instrument the sample is placed before the monochromator, whereas in the *Spectronic 20* instrument the sample is placed after it. [2]

### Question 2 [25]

- a) Atomic spectroscopy is a powerful tool available to the analyst today.
- (i) Two elements, X and Y are to be analyzed by flame AA and emission. The transition for element X is designated  $^2\text{S}_{1/2} \longrightarrow ^2\text{P}_{3/2}$  and has a wavelength of 852.1 nm. For Y, it is  $^1\text{S}_0 \longrightarrow ^1\text{S}_1$  at 228 nm. What is the ratio of excited to ground state atoms for each element, if the flame is operated at  $2250^\circ\text{C}$ ? [5]
  - (ii) Which of the two elements would be best analyzed by absorption, and why? [2]

- b) Atomic spectroscopic techniques have many applications in agriculture, especially in the area of mineral nutrition. Explain, with the aid of suitable diagrams and appropriate equations:
- the "Doppler Shift" and its effect on atomic spectra [4]
  - why in the determination of Zn and K in soils, emission is favored for K, whereas absorption is favored for Zn [3]
- c) Describe the path of a Ca atom (starting as off Ca Cl<sub>2</sub> solution) as soon as it enters the spray chamber in an AA instrument, up until it emits in flame emission spectrometry [6]
- d) With respect to Ca, explain chemical interference in flame atomic absorption spectrometry and explain how it is eliminated [5]

### Question 3 [25]

- a) Analytical chemists agree that the technique of atomic absorption came of age with the invention of the hollow cathode lamp by Sir Walsh in 1955.
- Draw and label the hollow cathode lamp [2]
  - Explain how the hollow cathode lamp works [2]
- b) There are several unique techniques employed by the agronomy laboratory at the Simunye Sugar Estate when using the Varian Spectr-AA-10 spectrophotometer. Explain:
- Why in the analysis of Sr, 100 ppm La is added to all solutions [2]
  - Why in the analysis of Cu, the instrument is operated under "standard additions" mode [2]
- c) A major breakthrough in atomic absorption spectrophotometry since the invention of the hollow cathode lamp is graphite furnace AA.
- What is the major structural difference between flame AA and graphite furnace AA? Use diagrams to support your answer [3]
  - Identify the physical stages involved in a furnace program and describe the processes that occur during each stage. At what stage is the signal sampled, and why? [5]
  - Outline three (3) advantages of graphite furnace AA over flame AA [3]
- d) In 2001, the Swaziland Water Services Corporation acquired a new atomic spectrometer called Liberty 110 ICP.
- What does ICP stands for? [1]
  - With the aid of a diagram briefly describe the ICP torch, how the ICP is initiated, and how it is maintained and stabilized. [3]
  - What are the normal operating values of the ICP in terms of:  
Power in kW----- Temperature in K----- [2]

**SECTION B****Chromatographic Techniques**

Answer any two questions from this section.

**Question 4 [25]**

- a) A typical GC instrument has several standard components, each of which is listed below. In each case give a brief description of the component, followed by its function.

- (i) Nitrogen Gas Cylinder [2]
- (ii) Filter Cartridge [2]
- (iii) Soap Bubble Flow Meter [2]
- (iv) Syringe [2]
- (v) Oven [2]

- b) One of the applications of GC is the separation of benzene from its mixture with cyclohexane, followed by quantification of the benzene. A typical output from the instrument is shown below:

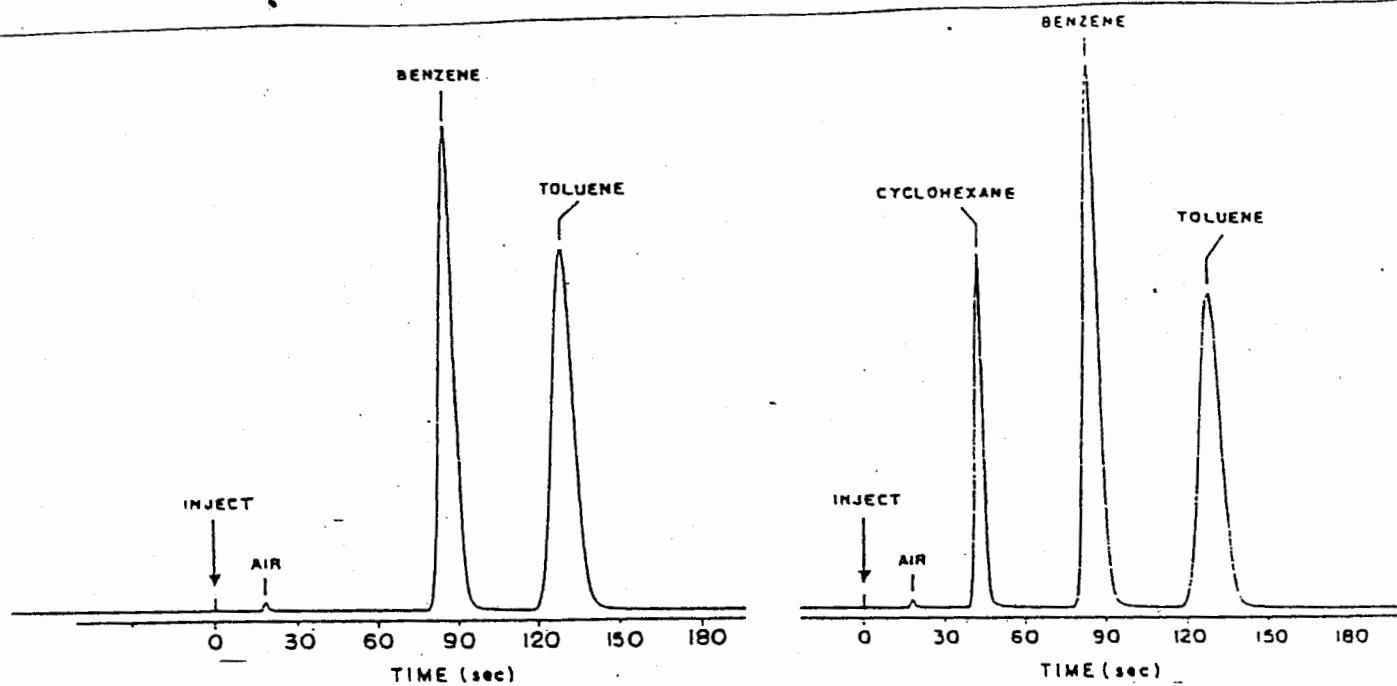


Figure IX-1. Gas chromatograms of injections of a standard mixture of benzene and toluene (left), and a sample containing cyclohexane and benzene with the internal standard toluene added (right).

- (i) In the experiment, explain the role of toluene ( explain how it serves this role) [3]
- (ii) Calculate the capacity factor of cyclohexane [3]
- (iii) Are the cyclohexane and benzene peaks properly resolved [3]

- (iv) Use the benzene peak in the sample chromatogram to calculate N; show how this value was obtained. [4]
- (v) Given that the column used was 10 m, calculate HETP in mm. [2]

### Question 5 [25]

- a) Use diagrams to describe the process of "elution" in chromatography [3]
- b) Describe each of the two ways by which elution is performed in GC [2]
- c) Sketch the Van Deemter plot for GC and indicate the region where mobile phase velocity is optimum for analysis [2]
- d) (i) What is meant by resistance to mass transfer in the mobile phase in GC? [3]  
 (ii) State the HETP equation for resistance to mass transfer in the mobile phase in GC [3]  
 (iii) What is meant by resistance by mass transfer in the stationary phase in GC [3]  
 (iv) State the HETP equation for resistance to mass transfer in stationary phase in GC [3]
- e) The following results were obtained in a GC experiment whereby two standards were prepared by weighing the pure compounds, followed by injection on to the GC. The sample (3.9786 g) was also injected following addition of toluene as indicated in the table. The peak areas were taken directly from the integrator.

	Wt. Of benzene (g)	Wt. Of toluene (g)	Peak area, benzene	Peak area, toluene
<b>STANDARD # 1</b>	0.5361	0.5023	35012	34754
<b>STANDARD # 2</b>	1.0026	0.5001	85600	36251
<b>UNKNOWN # 005</b>	?	0.5015	53620	35621

Draw an appropriate calibration on the graph paper provided, and use it to calculate the % benzene in unknown #005 [6]

### Question 6 [25]

- a) What is meant by the "race track" effect in chromatography, and how is it eliminated? [2]
- b) Sketch the Van Deemter plot for LC and explain how it is different from that of GC. [2]
- c) Use equations to describe the process of "silanization" in LC. [2]
- d) A typical LC instrument has several standard components, each of which is listed below. In each case give a brief description of the component, followed by its function.
- (i) Column [3]  
 (ii) Sample loop and injector [3]

- 
- e) Describe each of the two ways by which elution is performed in LC [2]
  - f)
    - (i) What is meant by longitudinal diffusion in chromatography? [3]
    - (ii) State the HETP equation for longitudinal diffusion in open tubes [2]
    - (iii) What is meant by Eddy Diffusion in chromatography? [3]
    - (iv) State the HETP equation for Eddy Diffusion in packed tubes [3]
-

## **1. PERIODIC CHART OF THE ELEMENTS**

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

#### 4. NET STABILITY CONSTANTS

CONSTANTS	
$\text{Ag}(\text{CN})_2^-$	$5 \times 10^{20}$
$\text{Ag}(\text{NH}_3)_2^+$	$1.6 \times 10^7$
$\text{Ag}(\text{S}_2\text{O}_3)_2^{-3}$	$4.7 \times 10^{13}$
$\text{Al}(\text{OH})_4^-$	$1.0 \times 10^{33}$
$\text{Ca}(\text{EDTA})$	$1.0 \times 10^{11}$
$\text{Cd}(\text{CN})_4^-$	$8.3 \times 10^{17}$
$\text{Cd}(\text{NH}_3)_4^{++}$	$5.5 \times 10^6$
$\text{Co}(\text{NH}_3)_6^{+3}$	$2 \times 10^{35}$
$\text{Cr}(\text{OH})_4^-$	$4 \times 10^{28}$
$\text{Cu}(\text{CN})_4^{-3}$	$1 \times 10^{23}$
$\text{Cu}(\text{NH}_3)_4^{++}$	$1.2 \times 10^{11}$
$\text{Fe}(\text{CN})_6^{-3}$	$4.0 \times 10^{43}$
$\text{Fe}(\text{CN})_6^{-4}$	$2.5 \times 10^{35}$
$\text{Fe}(\text{SCN})^{++}$	$1.0 \times 10^3$
$\text{HgCl}_4^-$	$1.3 \times 10^{15}$
$\text{Hg}(\text{CN})_4^-$	$8.3 \times 10^{38}$
$\text{Hg}(\text{SCN})_4^-$	$5.0 \times 10^{20}$
$\text{HgI}_4^-$	$6.3 \times 10^{29}$
$\text{Mg}(\text{EDTA})$	$1.3 \times 10^9$
$\text{Ni}(\text{NH}_3)_4^{++}$	$4.7 \times 10^7$
$\text{Pb}(\text{OH})_3^-$	$7.9 \times 10^{13}$
$\text{Zn}(\text{CN})_4^-$	$4.2 \times 10^{16}$
$\text{Zn}(\text{NH}_3)_4^{++}$	$7.8 \times 10^8$
$\text{Zn}(\text{OH})_4^-$	$6.3 \times 10^{14}$

— 1 —

58 <b>Ce</b> 140.12	59 <b>Pr</b> 140.9077	60 <b>Nd</b> 144.24	61 <b>Pm</b> (145)	62 <b>Sm</b> 150.36	63 <b>Eu</b> 151.96	64 <b>Gd</b> 157.25	65 <b>Tb</b> 158.9254	66 <b>Dy</b> 162.50	67 <b>Ho</b> 164.9304	68 <b>Er</b> 167.26	69 <b>Tm</b> 168.9342	70 <b>Yb</b> 173.04	71 <b>Lu</b> 174.967
90 <b>Th</b> 232.0381	91 <b>Pa</b> 231.0351	92 <b>U</b> 238.0289	93 <b>Np</b> 237.0482	94 <b>Pu</b> (241)	95 <b>Am</b> (243)	96 <b>Cm</b> (247)	97 <b>Bk</b> (247)	98 <b>Cf</b> (251)	99 <b>Es</b> (252)	100 <b>Fm</b> (257)	101 <b>Md</b> (258)	102 <b>No</b> (259)	103 <b>Lr</b> (260)

**▲ Actinide series**

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## 2. IONIZATION CONST.

Acetic	$1.9 \times 10^{-5}$	Hypochlorous	$3.7 \times 10^{-8}$
-Amino-		$\text{H}_2\text{S}$	$\text{K}_1 9 \times 10^{-8}$
pyridinium Ion	$2 \times 10^{-7}$		$\text{K}_2 1 \times 10^{-15}$
Ammonium Ion	$5.6 \times 10^{-10}$	Imidazolium Ion	$1.1 \times 10^{-7}$
Linilinium Ion	$2.3 \times 10^{-5}$	Lactic	$1.4 \times 10^{-4}$
Arsenic	$\text{K}_1 5.6 \times 10^{-3}$	Methylammonium	
Benzoic	$6.7 \times 10^{-5}$	Ion	$2.7 \times 10^{-11}$
Boric	$\text{K}_1 5 \times 10^{-10}$	Monoethanol-	
Carbonic	$\text{K}_1 4.3 \times 10^{-7}$	ammonium Ion	$3 \times 10^{-10}$
	$\text{K}_2 5.6 \times 10^{-11}$	Nicotinium Ion	$9.6 \times 10^{-9}$
Chloroacetic	$1.5 \times 10^{-3}$	Oxalic	$\text{K}_1 6 \times 10^{-2}$
Chromic	$\text{K}_2 3.2 \times 10^{-7}$		$\text{K}_2 6 \times 10^{-5}$
Citric	$\text{K}_1 8.7 \times 10^{-4}$	Phenol	$1.3 \times 10^{-10}$
	$\text{K}_2 1.8 \times 10^{-5}$	Phthalic	$\text{K}_2 4 \times 10^{-8}$
Dichloroacetic	$\text{K}_3 4 \times 10^{-6}$	Phosphoric	$\text{K}_1 7.5 \times 10^{-3}$
EDTA	$5 \times 10^{-2}$		$\text{K}_2 6.2 \times 10^{-8}$
	$\text{K}_1 7 \times 10^{-3}$		$\text{K}_3 4.7 \times 10^{-13}$
	$\text{K}_2 2 \times 10^{-3}$	Phosphorous	$\text{K}_1 1.0 \times 10^{-2}$
	$\text{K}_3 7 \times 10^{-7}$		$\text{K}_2 2.6 \times 10^{-7}$
Formic	$\text{K}_4 6 \times 10^{-11}$	Pyridinium Ion	$1 \times 10^{-5}$
$\alpha$ -D(+)-Glucose	$2 \times 10^{-4}$	Succinic	$\text{K}_1 7 \times 10^{-5}$
Glycinium Ion	$5.2 \times 10^{-13}$		$\text{K}_2 2.5 \times 10^{-6}$
$\text{K}_1$	$4.6 \times 10^{-3}$	Sulfuric	$\text{K}_2 1.2 \times 10^{-2}$
	$2.5 \times 10^{-10}$	Sulfurous	$\text{K}_1 2 \times 10^{-2}$
Hydrazinium Ion	$5.9 \times 10^{-9}$		$\text{K}_2 6 \times 10^{-8}$
Hydrocyanic	$7 \times 10^{-10}$	Trimethyl-	
Hydrofluoric	$7 \times 10^{-4}$	ammonium Ion	$1.6 \times 10^{-10}$
Hydroxyl-		Uric	$1.3 \times 10^{-4}$
ammonium Ion	$9.1 \times 10^{-7}$	Water, K <sub>w</sub> , 24°C	$1.0 \times 10^{-14}$

### **3. SOLUBILITY PRODUCT CONSTANTS**

$\text{gBr}$	$4 \times 10^{-13}$	$\text{BaC}_2\text{O}_4$	$2 \times 10^{-8}$	$\text{KClO}_4$	$2 \times 10^{-2}$
$\text{g}_2\text{CO}_3$	$6 \times 10^{-12}$	$\text{BaSO}_4$	$1 \times 10^{-10}$	$\text{MgCO}_3$	$1 \times 10^{-5}$
$\text{gCl}$	$1 \times 10^{-10}$	$\text{CaCO}_3$	$5 \times 10^{-9}$	$\text{MgC}_2\text{O}_4$	$9 \times 10^{-5}$
$\text{g}_2\text{CrO}_4$	$2 \times 10^{-12}$	$\text{CaF}_2$	$4 \times 10^{-11}$	$\text{MgNH}_4\text{PO}_4$	$2 \times 10^{-13}$
$\text{g}[\text{Ag}(\text{CN})_2]$	$4 \times 10^{-12}$	$\text{CaC}_2\text{O}_4$	$2 \times 10^{-9}$	$\text{Mg}(\text{OH})_2$	$1 \times 10^{-11}$
$\text{gI}$	$1 \times 10^{-16}$	$\text{CdS}$	$1 \times 10^{-28}$	$\text{MnS}$	$1 \times 10^{-15}$
$\text{g}_3\text{PO}_4$	$1 \times 10^{-19}$	$\text{Cu}(\text{OH})_2$	$2 \times 10^{-20}$	$\text{PbCrO}_4$	$2 \times 10^{-14}$
$\text{g}_2\text{S}$	$1 \times 10^{-50}$	$\text{CuS}$	$1 \times 10^{-36}$	$\text{PbS}$	$1 \times 10^{-28}$
$\text{gCNS}$	$1 \times 10^{-12}$	$\text{Fe(OH)}_3$	$1 \times 10^{-36}$	$\text{PbSO}_4$	$2 \times 10^{-8}$
$\text{l}(\text{OH})_3$	$2 \times 10^{-32}$	$\text{Hg}_2\text{Br}_2$	$3 \times 10^{-23}$	$\text{SrCrO}_4$	$4 \times 10^{-5}$
$\text{aCO}_3$	$5 \times 10^{-9}$	$\text{Hg}_2\text{Cl}_2$	$6 \times 10^{-19}$	$\text{Zn}(\text{OH})_2$	$3.6 \times 10^{-10}$
$\text{aCrO}_4$	$1 \times 10^{-10}$	$\text{HgS}$	$1 \times 10^{-52}$	$\text{ZnS}$	$1 \times 10^{-24}$

## 5. FIRST IONIZATION ENERGIES, e.v.

IA	2A	14							3A	4A	5A	6A	7A	2B			
5.4	9.3								8.3	11	15	14	17	22			
5.1	7.6	3B	4B	5B	6B	7B	8B	1B	2B	6.0	8.1	11	10	13	16		
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	14
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	13
3.9	5.2	5.0	5.5	6	8.0	7.9	8.7	9.2	9.0	9.2	10	6.1	7.4	8		11	

### 6. ELECTRONEGATIVITIES, Pauling

IA		2A		2.1		3A		4A		5A		6A		7A		
1.0	1.5					2.0	2.5	3.0	3.5	4.0						
0.9	1.2	3B	4B	5B	6B	7B	BB	1B	2B	1.5	1.8	2.1	2.5	3.0		
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	2.8
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	2.5
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

143 141 137 135 133 1

## 9. LATTICE ENERGIES

(All negative)		kJ/mol		
	F	Cl	Br	I
Li	1030	840	781	718
Na	914	770	728	687
K	812	701	671	633
Rb	780	682	654	617
Cs	744	630	613	584

10. HALF LIVES

10. HALF LIVES			
H <sup>3</sup>	12.3 years	K <sup>40</sup>	$1.28 \times 10^9$ y
F <sup>20</sup>	11.4 secs	Ca <sup>45</sup>	165 days
C <sup>14</sup>	5730 years	Fe <sup>59</sup>	45 days
Na <sup>24</sup>	15.0 hours	Co <sup>60</sup>	5.26 y
P <sup>32</sup>	14.3 days	Br <sup>82</sup>	35.5 hours
S <sup>35</sup>	88 days	Sr <sup>90</sup>	28 years
Cl <sup>36</sup>	$3.1 \times 10^5$ y	I <sup>129</sup>	$1.7 \times 10^7$ y
		I <sup>131</sup>	8.1 days
		Cs <sup>137</sup>	30 years
		Au <sup>198</sup>	2.69 day
		Ra <sup>220</sup>	1620 yrs
		U <sup>235</sup>	$7.1 \times 10^8$ y
		U <sup>238</sup>	$4.51 \times 10^{10}$ y
		Pu <sup>230</sup>	24,400 y

**11. ACID-BASE INDICATORS AT 25°C**

Indicator	pH range	pK <sub>in</sub>	Acid	Base
hymol blue	1.2 - 2.8	1.6	red	yellow
ethyl yellow	2.9 - 4.0	3.3	red	yellow
ethyl orange	3.1 - 4.4	4.2	red	yellow
romocresol green	3.8 - 5.4	4.7	yellow	blue
ethyl red	4.2 - 6.2	5.0	red	yellow
chlorophenol red	4.8 - 6.4	6.0	yellow	red
romothymol blue	6.0 - 7.6	7.1	yellow	blue
henol red	6.4 - 8.0	7.4	yellow	red
resol purple	7.4 - 9.0	8.3	yellow	purple
hymol blue	8.0 - 9.6	8.9	yellow	blue
henolphthalein	8.0 - 9.8	9.7	colorless	red
hymolphthalein	9.3 - 10.5	9.9	colorless	blue

**12. ELECTRODE POTENTIALS, E°**

$a^+ + e \rightleftharpoons Na$	- 2.713
$g^{**} + 2e \rightleftharpoons Mg$	- 2.37
$I^{***} + 3e \rightleftharpoons Al$	- 1.66
$r^{**} + 2e \rightleftharpoons Zn$	- 0.763
$e^{**} + 2e \rightleftharpoons Fe$	- 0.44
$I^{**} + 2e \rightleftharpoons Cd$	- 0.403
$r^{***} + e \rightleftharpoons Cr^{**}$	- 0.38
$I^+ + e \rightleftharpoons Ti^{**}$	- 0.336
$r^{**} + e \rightleftharpoons V^{**}$	- 0.255
$r^{**} + 2e \rightleftharpoons Sn$	- 0.14
$b^{**} + 2e \rightleftharpoons Pb$	- 0.126
$I^+ + 2e \rightleftharpoons H_2$	0.000
$O_6^{= -} + 2e \rightleftharpoons 2S_2O_3^{= -}$	0.09
$O_6^{= -} + 2H^+ + e \rightleftharpoons Ti^{***} + H_2O$	0.10
$+ 2H^+ + 2e \rightleftharpoons H_2S$	0.14
$a^{**} + 2e \rightleftharpoons Sn^{**}$	0.14
$u^{**} + e \rightleftharpoons Cu^+$	0.17
$O_4^{= -} + 4H^+ + 2e \rightleftharpoons H_2O + H_2SO_3$	0.17
$gCl + e \rightleftharpoons Cl^- + Ag$	0.222
satuated calomel	(0.244)
$g_2Cl_2 + 2e \rightleftharpoons 2Cl^- + 2Hg$	0.268
$i^{***} + 3e \rightleftharpoons Bi$	0.293
$O_2^{= -} + 4H^+ + 2e \rightleftharpoons U^{**} + 2H_2O$	0.33
$O^{**} + 2H^+ + e \rightleftharpoons V^{**} + H_2O$	0.34
$u^{**} + 2e \rightleftharpoons Cu$	0.34
$e(CN)_6^{= -3} + e \rightleftharpoons Fe(CN)_6^{= -4}$	0.355
$u^+ + e \rightleftharpoons Cu$	0.52
$r^- + 2e \rightleftharpoons 3I^-$	0.545
$AsO_4^{= -} + 2H^+ + 2e \rightleftharpoons H_3AsO_3 + H_2O$	0.56
$+ 2e \rightleftharpoons 2I^-$	0.621
$HgCl_2 + 2e \rightleftharpoons Hg_2Cl_2 + 2Cl^-$	0.63
$I_2 + 2H^+ + 2e \rightleftharpoons H_2O_2$	0.69
$quinone + 2H^+ + 2e \rightleftharpoons Hydroquinone$	0.70
$e^{***} + e \rightleftharpoons Fe^{**}$	0.771
$Ig_2^{**} + 2e \rightleftharpoons 2Hg$	0.792
$g^+ + e \rightleftharpoons Ag$	0.799
$Ig^{**} + 2e \rightleftharpoons Hg$	0.851
$Hg^{**} + 2e \rightleftharpoons Hg_2^{**}$	0.907
$IO_3^- + 3H^+ + 2e \rightleftharpoons HNO_2 + H_2O$	0.94
$INO_2 + H^+ + e \rightleftharpoons NO + H_2O$	0.98
$VO_2^+ + 2H^+ + e \rightleftharpoons VO^{**} + H_2O$	0.999
$Ir_2 + 2e \rightleftharpoons 2Br^-$	1.08
$IO_3^- + 12H^+ + 10e \rightleftharpoons 6H_2O + I_2$	1.19
$I_2 + 4H^+ + 4e \rightleftharpoons 2H_2O$	1.229
$MnO_4^- + 4H^+ + 2e \rightleftharpoons Mn^{**} + 2H_2O$	1.23
$Ir_2O_7^- + 14H^+ + 6e \rightleftharpoons 7H_2O + 2Cr^{**}$	1.33
$I_2 + 2e \rightleftharpoons 2Cl^-$	1.358
$BrO_3^- + 12H^+ + 10e \rightleftharpoons 6H_2O + Br_2$	1.50
$MnO_4^- + 8H^+ + 5e \rightleftharpoons 4H_2O + Mn^{**}$	1.51
$e^{**} + e \rightleftharpoons Ce^{**}$	1.61

**13. MEAN ACTIVITY COEFFICIENTS**

M	KCl	Na <sub>2</sub> SO <sub>4</sub>	ZnSO <sub>4</sub>
0.001	0.965	0.89	0.70
0.01	0.901	0.72	0.39
0.1	0.760	0.45	0.15

**14. DATA REJECTION—Q TABLE**

n	Q <sub>90</sub>	n	Q <sub>90</sub>	n	Q <sub>90</sub>
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 <sup>-1</sup> at 25°C (i.e. Bond Energies)						
Ssingle	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	251	H—H	436	C=C	615	
F	327	N≡N	946	C≡C	812	
Cl	271	N=O	607	C=O	749	

D.F.	t <sub>50</sub>	t <sub>90</sub>	t <sub>95</sub>	t <sub>99</sub>	t <sub>99.9</sub>
1	1.0	6.3	13	64	
2	0.82	2.9	4.3	9	
3	0.76	2.35	3.2	5	
4	0.74	2.13	2.8	4	
5	0.73	2.02	2.57	4	
6	0.72	1.94	2.45	3	
7	0.71	1.90	2.36	3	
8	0.71	1.86	2.31	3	
9	0.70	1.83	2.26	3	
10	0.70	1.81	2.23	3	
20	0.69	1.72	2.09	2	
30	0.68	1.70	2.04	2	
∞	0.67	1.64	1.96	2	

**16. HEATS OF FORMATION**

$\Delta H^\circ$  in kJ mol<sup>-1</sup> at 25°C  
All ions in H<sub>2</sub>O solution except as noted

All Elements = 0

H <sub>g</sub>	218	H <sup>+</sup>	0.0	H <sub>2</sub> O <sub>g</sub>	-242
O <sub>g</sub>	249	Na <sup>+</sup>	-240	H <sub>2</sub> O <sub>l</sub>	-286
C <sub>g</sub>	717	Ag <sup>+</sup>	106	CO <sub>g</sub>	-111
N <sub>g</sub>	473	NH <sub>4</sub> <sup>+</sup>	-133	CO <sub>2g</sub>	-394
F <sub>g</sub>	79	OH <sup>-</sup>	-230	NH <sub>3g</sub>	-46
Cl <sub>g</sub>	122	F <sup>-</sup>	-333	NO <sub>g</sub>	90
Br <sub>g</sub>	112	Cl <sup>-</sup>	-167	NO <sub>2g</sub>	33
I <sub>g</sub>	107	Br <sup>-</sup>	-122	N <sub>2</sub> O <sub>4g</sub>	9
S <sub>g</sub>	279	I <sup>-</sup>	-55	SO <sub>2g</sub>	-297
P <sub>g</sub>	315	S=	33	SO <sub>3g</sub>	-396
Na <sub>g</sub>	107	SO <sub>4=</sub>	-909	H <sub>2</sub> S <sub>g</sub>	-21
K <sub>g</sub>	88	CO <sub>3=</sub>	-677	NaF <sub>g</sub>	-574
Na <sup>+</sup>	609	HF <sub>g</sub>	-271	NaCl <sub>g</sub>	-411
K <sup>+</sup>	514	HC <sub>l</sub> <sub>g</sub>	-92	KF <sub>g</sub>	-567
F <sub>g</sub>	255	HBr <sub>g</sub>	-36	KCl <sub>g</sub>	-437
Cl <sub>g</sub>	233	HI <sub>g</sub>	26	AgCl <sub>g</sub>	-127
CH <sub>4g</sub>	75	HCN <sub>g</sub>	135	AgBr <sub>g</sub>	-100
C <sub>2</sub> H <sub>2g</sub>	227	PH <sub>3g</sub>	5	PCl <sub>3g</sub>	-287
C <sub>2</sub> H <sub>4g</sub>	52	C <sub>6</sub> H <sub>6g</sub>	49	PCl <sub>5g</sub>	-375
C <sub>2</sub> H <sub>6g</sub>	-85	CH <sub>3</sub> OH <sub>l</sub>	-238		
C <sub>3</sub> H <sub>8g</sub>	-105	C <sub>2</sub> H <sub>5</sub> OH <sub>l</sub>	-235		
nC <sub>4</sub> H <sub>10g</sub>	-127	C <sub>2</sub> H <sub>5</sub> OH <sub>l</sub>	-278		
nC <sub>8</sub> H <sub>18g</sub>	-209	COCl <sub>2g</sub>	-219		
CCl <sub>4g</sub>	-135	CH <sub>3</sub> Cl <sub>g</sub>	-81		

**17. ABS. ENTROPY S°**

J mol <sup>-1</sup> K <sup>-1</sup> at 25°C		
H <sub>g</sub>	131	P <sub>4</sub> <sub>wh</sub>
N <sub>2g</sub>	192	HF <sub>g</sub>
O <sub>2g</sub>	205	HC <sub>l</sub> <sub>g</sub>
Cl <sub>g</sub>	223	H <sub>2</sub> O <sub>g</sub>
F <sub>g</sub>	203	CO <sub>g</sub>
C <sub>g</sub>	5.7	CO <sub>2g</sub>
S <sub>g</sub>	254	SO <sub>2g</sub>
CH <sub>4g</sub>	186	SO <sub>3g</sub>
C <sub>2</sub> H <sub>6g</sub>	229	BF <sub>3g</sub>
C <sub>3</sub> H <sub>8g</sub>	270	CH <sub>3</sub> OH <sub>l</sub>
C <sub>2</sub> H <sub>2g</sub>	201	C <sub>2</sub> H <sub>5</sub> OH <sub>l</sub>
C <sub>2</sub> H <sub>4g</sub>	219	(CH <sub>3</sub> ) <sub>2</sub> O <sub>g</sub>
C <sub>6</sub> H <sub>6g</sub>	269	CH <sub>3</sub> COOH <sub>l</sub>

**18. ΔG° FORMATION**

kJ mol <sup>-1</sup> at 25°C		
H <sub>g</sub>	203	HF <sub>g</sub>
F <sub>g</sub>	62	HC <sub>l</sub> <sub>g</sub>
Cl <sub>g</sub>	106	HBr <sub>g</sub>
O <sub>g</sub>	232	HI <sub>g</sub>
NO <sub>g</sub>	87	NH <sub>3g</sub>
NO <sub>2g</sub>	51	CO <sub>g</sub>
N <sub>2</sub> O <sub>4g</sub>	98	CO <sub>2g</sub>
C <sub>2</sub> H <sub>4g</sub>	68	C <sub>2</sub> H <sub>2g</sub>
C <sub>6</sub> H <sub>6g</sub>	125	CH <sub>3</sub> OH <sub>l</sub>
CCl <sub>4g</sub>	-65	C <sub>2</sub> H <sub>5</sub> OH <sub>l</sub>
BF <sub>3g</sub>	-1120	CHCl <sub>3g</sub>

**20. CONC. ACIDS AND BASES**

M.W.
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