

Table 4-1 Ordinate and area for the normal (Gaussian) error curve,

$$y = \frac{1}{\sqrt{2\pi}} e^{-z^2/2}$$

$ z ^a$	y	Area ^b	$ z $	y	Area	$ z $	y	Area
0.0	0.398 9	0.000 0	1.4	0.149 7	0.419 2	2.8	0.007 9	0.497 4
0.1	0.397 0	0.039 8	1.5	0.129 5	0.433 2	2.9	0.006 0	0.498 1
0.2	0.391 0	0.079 3	1.6	0.110 9	0.445 2	3.0	0.004 4	0.498 650
0.3	0.381 4	0.117 9	1.7	0.094 1	0.455 4	3.1	0.003 3	0.499 032
0.4	0.368 3	0.155 4	1.8	0.079 0	0.464 1	3.2	0.002 4	0.499 313
0.5	0.352 1	0.191 5	1.9	0.065 6	0.471 3	3.3	0.001 7	0.499 517
0.6	0.333 2	0.225 8	2.0	0.054 0	0.477 3	3.4	0.001 2	0.499 663
0.7	0.312 3	0.258 0	2.1	0.044 0	0.482 1	3.5	0.000 9	0.499 767
0.8	0.289 7	0.288 1	2.2	0.035 5	0.486 1	3.6	0.000 6	0.499 841
0.9	0.266 1	0.315 9	2.3	0.028 3	0.489 3	3.7	0.000 4	0.499 904
1.0	0.242 0	0.341 3	2.4	0.022 4	0.491 8	3.8	0.000 3	0.499 928
1.1	0.217 9	0.364 3	2.5	0.017 5	0.493 8	3.9	0.000 2	0.499 952
1.2	0.194 2	0.384 9	2.6	0.013 6	0.495 3	4.0	0.000 1	0.499 968
1.3	0.171 4	0.403 2	2.7	0.010 4	0.496 5			

Table 4-6 Values of Q for rejection of data

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

Table 4-2 Values of Student's t

Degrees of freedom	Confidence level (%)						
	50	90	95	98	99	99.5	99.9
1	1.000	6.314	12.706	31.821	63.657	127.32	636.619
2	0.816	2.920	4.303	6.965	9.925	14.089	31.598
3	0.765	2.353	3.182	4.541	5.841	7.453	12.924
4	0.741	2.132	2.776	3.747	4.604	5.598	8.610
5	0.727	2.015	2.571	3.365	4.032	4.773	6.869
6	0.718	1.943	2.447	3.143	3.707	4.317	5.959
7	0.711	1.895	2.365	2.998	3.500	4.029	5.408
8	0.706	1.860	2.306	2.896	3.355	3.832	5.041
9	0.703	1.833	2.262	2.821	3.250	3.690	4.781
10	0.700	1.812	2.228	2.764	3.169	3.581	4.587
15	0.691	1.753	2.131	2.602	2.947	3.252	4.073
20	0.687	1.725	2.086	2.528	2.845	3.153	3.850
25	0.684	1.708	2.060	2.485	2.787	3.078	3.725
30	0.683	1.697	2.042	2.457	2.750	3.030	3.646
40	0.681	1.684	2.021	2.423	2.704	2.971	3.551
60	0.679	1.671	2.000	2.390	2.660	2.915	3.460
120	0.677	1.658	1.980	2.358	2.617	2.860	3.373
∞	0.674	1.645	1.960	2.326	2.576	2.807	3.291

Table 4-5 Critical values of $F = s_1^2/s_2^2$ at 95% confidence level

Degrees of freedom for s_2	Degrees of freedom for s_1													
	2	3	4	5	6	7	8	9	10	12	15	20	30	∞
2	19.0	19.2	19.2	19.3	19.3	19.4	19.4	19.4	19.4	19.4	19.4	19.4	19.5	19.5
3	9.55	9.28	9.12	9.01	8.94	8.89	8.84	8.81	8.79	8.74	8.70	8.66	8.62	8.53
4	6.94	6.59	6.39	6.26	6.16	6.09	6.04	6.00	5.96	5.91	5.86	5.80	5.75	5.63
5	5.79	5.41	5.19	5.05	4.95	4.88	4.82	4.77	4.74	4.68	4.62	4.56	4.50	4.36
6	5.14	4.76	4.53	4.39	4.28	4.21	4.15	4.10	4.06	4.00	3.94	3.87	3.81	3.67
7	4.74	4.35	4.12	3.97	3.87	3.79	3.73	3.68	3.64	3.58	3.51	3.44	3.38	3.23
8	4.46	4.07	3.84	3.69	3.58	3.50	3.44	3.39	3.35	3.28	3.22	3.15	3.08	2.93
9	4.26	3.86	3.63	3.48	3.37	3.29	3.23	3.18	3.14	3.07	3.01	2.94	2.86	2.71
10	4.10	3.71	3.48	3.33	3.22	3.14	3.07	3.02	2.98	2.91	2.84	2.77	2.70	2.54
11	3.98	3.59	3.36	3.20	3.10	3.01	2.95	2.90	2.85	2.79	2.72	2.65	2.57	2.40
12	3.88	3.49	3.26	3.11	3.00	2.91	2.85	2.80	2.75	2.69	2.62	2.54	2.47	2.30
13	3.81	3.41	3.18	3.02	2.92	2.83	2.77	2.71	2.67	2.60	2.53	2.46	2.38	2.21
14	3.74	3.34	3.11	2.96	2.85	2.76	2.70	2.65	2.60	2.53	2.46	2.39	2.31	2.13
15	3.68	3.29	3.06	2.90	2.79	2.71	2.64	2.59	2.54	2.48	2.40	2.33	2.25	2.07
16	3.63	3.24	3.01	2.85	2.74	2.66	2.59	2.54	2.49	2.42	2.35	2.28	2.19	2.01
17	3.59	3.20	2.96	2.81	2.70	2.61	2.55	2.49	2.45	2.38	2.31	2.23	2.15	1.96
18	3.56	3.16	2.93	2.77	2.66	2.58	2.51	2.46	2.41	2.34	2.27	2.19	2.11	1.92
19	3.52	3.13	2.90	2.74	2.63	2.54	2.48	2.42	2.38	2.31	2.23	2.16	2.07	1.88
20	3.49	3.10	2.87	2.71	2.60	2.51	2.45	2.39	2.35	2.28	2.20	2.12	2.04	1.84
30	3.32	2.92	2.69	2.53	2.42	2.33	2.27	2.21	2.16	2.09	2.01	1.93	1.84	1.62
∞	3.00	2.60	2.37	2.21	2.10	2.01	1.94	1.88	1.83	1.75	1.67	1.57	1.46	1.00

Exam 1 – Chem 454 – February 9, 2007 – 100 total points

Name: _____

Table 14-2 Reduction potentials of biological interest

Reaction	E° (V)	$E^{\circ'}$ (V)
$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$	+1.229	+0.816
$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$	+0.771	+0.771
$I_2 + 2e^- \rightleftharpoons 2I^-$	+0.535	+0.535
Cytochrome <i>a</i> (Fe^{3+}) + $e^- \rightleftharpoons$ cytochrome <i>a</i> (Fe^{2+})	+0.290	+0.290
$O_2(g) + 2H^+ + 2e^- \rightleftharpoons H_2O_2$	+0.695	+0.281
Cytochrome <i>c</i> (Fe^{3+}) + $e^- \rightleftharpoons$ cytochrome <i>c</i> (Fe^{2+})	—	+0.254
2,6-Dichlorophenolindophenol + $2H^+ + 2e^- \rightleftharpoons$ reduced 2,6-dichlorophenolindophenol	—	+0.22
Dehydroascorbate + $2H^+ + 2e^- \rightleftharpoons$ ascorbate + H_2O	+0.390	+0.058
Fumarate + $2H^+ + 2e^- \rightleftharpoons$ succinate	+0.433	+0.031
Methylene blue + $2H^+ + 2e^- \rightleftharpoons$ reduced product	+0.532	+0.011
Glyoxylate + $2H^+ + 2e^- \rightleftharpoons$ glycolate	—	-0.090
Oxaloacetate + $2H^+ + 2e^- \rightleftharpoons$ malate	+0.330	-0.102
Pyruvate + $2H^+ + 2e^- \rightleftharpoons$ lactate	+0.224	-0.190
Riboflavin + $2H^+ + 2e^- \rightleftharpoons$ reduced riboflavin	—	-0.208
$FAD + 2H^+ + 2e^- \rightleftharpoons FADH_2$	—	-0.219
(Glutathione-S) ₂ + $2H^+ + 2e^- \rightleftharpoons$ 2 glutathione-SH	—	-0.23
Safranin T + $2e^- \rightleftharpoons$ leucosafranin T	-0.235	-0.289
$(C_6H_5S)_2 + 2H^+ + 2e^- \rightleftharpoons$ 2C ₆ H ₅ SH	—	-0.30
$NAD^+ + H^+ + 2e^- \rightleftharpoons NADH$	-0.105	-0.320
$NADP^+ + H^+ + 2e^- \rightleftharpoons NADPH$	—	-0.324
Cystine + $2H^+ + 2e^- \rightleftharpoons$ 2 cysteine	—	-0.340
Acetoacetate + $2H^+ + 2e^- \rightleftharpoons$ L-β-hydroxybutyrate	—	-0.346
Xanthine + $2H^+ + 2e^- \rightleftharpoons$ hypoxanthine + H_2O	—	-0.371
$2H^+ + 2e^- \rightleftharpoons H_2$	0.000	-0.414
Gluconate + $2H^+ + 2e^- \rightleftharpoons$ glucose + H_2O	—	-0.44
$SO_4^{2-} + 2e^- + 2H^+ \rightleftharpoons SO_3^{2-} + H_2O$	—	-0.454
$2SO_3^{2-} + 2e^- + 4H^+ \rightleftharpoons S_2O_4^{2-} + 2H_2O$	—	-0.527

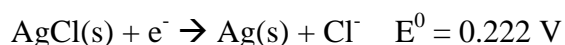
1] (5 points) Rank the following in terms of increasing reducing power

NADH, Fe^{3+} , Fe^{2+} , lactate

Weakest → Strongest _____

2] (5 points) What is E°_{cell} for $2I^- + 2H^+ \rightarrow H_2 + I_2$, is this a spontaneous reaction?

3] (10 points) The potential of the Ag/AgCl reference electrode is 0.197 volts. Given the standard reduction potential:



Calculate the concentration of KCl in this electrode.

4] Sketch a signal-concentration diagram clearly illustrating the concepts of sensitivity, detection limit and back ground. (15 points)

5] (25 points) Draw a Jablonski diagram clearly illustrating the following processes.

- a) absorption
- b) emission
- c) fluorescence
- d) phosphorescence
- e) vibrational relaxation
- f) external conversion
- g) internal conversion
- h) intersystem crossing

6] (5 points) Which of the transitions above are considered radiationless decays?

7] (10 points) What is the 95% confidence limit for the following set of data.

4.88, 5.13, 4.92, 5.22, 5.07, 4.72

8] The response of a Cl^- ISE electrode was a -455 mV in a solution of 4.33×10^{-3} M KCl. An unknown solution gave a potential -474 mV. What is $[\text{Cl}^-]$ of this unknown? (10 points)

9] An ASV analysis was conducted on a sample containing cadmium. A 1.00 g sample was dissolved in 100.0 mL of nitric acid. A 50.0 mL aliquot gave an ASV signal of $5.00 \mu\text{A}$. On the other 50.0 mL aliquot was added a spike of $10.0 \mu\text{L}$ of 1.00×10^{-2} M CdCl_2 and gave a signal of $6.00 \mu\text{A}$. What is concentration of Cd (AW 112.411 g/mol) in the sample in ppm? (15 points)

Answers

1] (5 points) Rank the following in terms of increasing reducing power

NADH, Fe^{3+} , Fe^{2+} , lactate

Weakest \rightarrow Strongest _____

Fe^{3+} , Fe^{2+} , lactate, NADH

2] (5 points) What is E^0_{cell} for $2\text{I}^- + 2\text{H}^+ \rightarrow \text{H}_2 + \text{I}_2$, is this a spontaneous reaction?

Cathode: $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$ $E^0 = 0.00$

Anode: $2\text{I}^- \rightarrow \text{I}_2 + 2\text{e}^-$ $E^0 = 0.535 \text{ V}$

$E^0_{\text{cell}} = E^0_{\text{cat}} - E^0_{\text{anod}} = 0.00 - 0.535 = -0.535 \text{ V}$, this is an uphill reaction

3] (10 points) The potential of the Ag/AgCl reference electrode is 0.197 volts. Given the standard reduction potential:

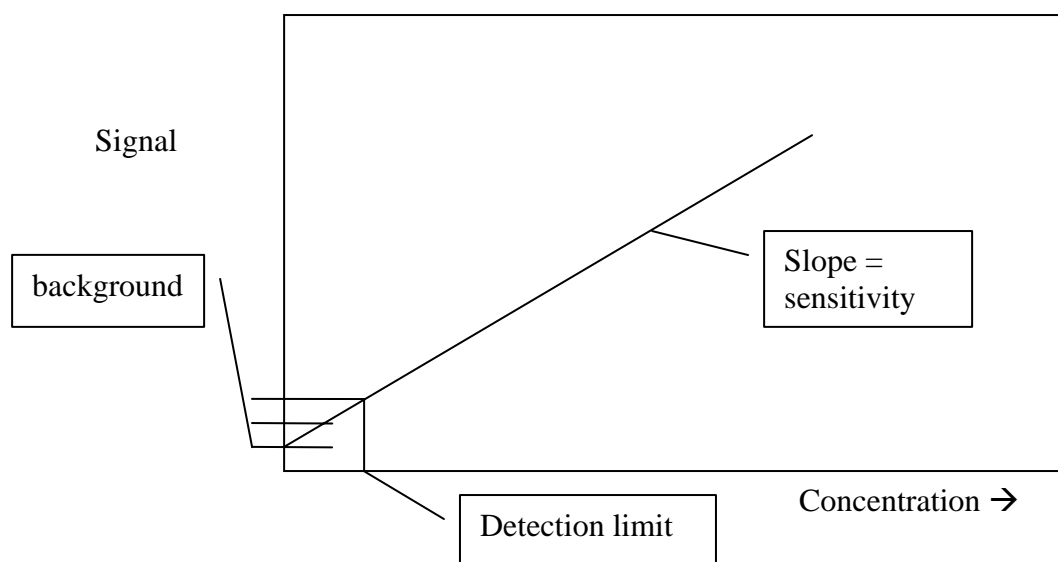
$\text{AgCl}(\text{s}) + \text{e}^- \rightarrow \text{Ag}(\text{s}) + \text{Cl}^-$ $E^0 = 0.222 \text{ V}$

Calculate the concentration of KCl in this electrode.

$E = 0.222 - 0.0592 \log [\text{Cl}^-] = 0.197$

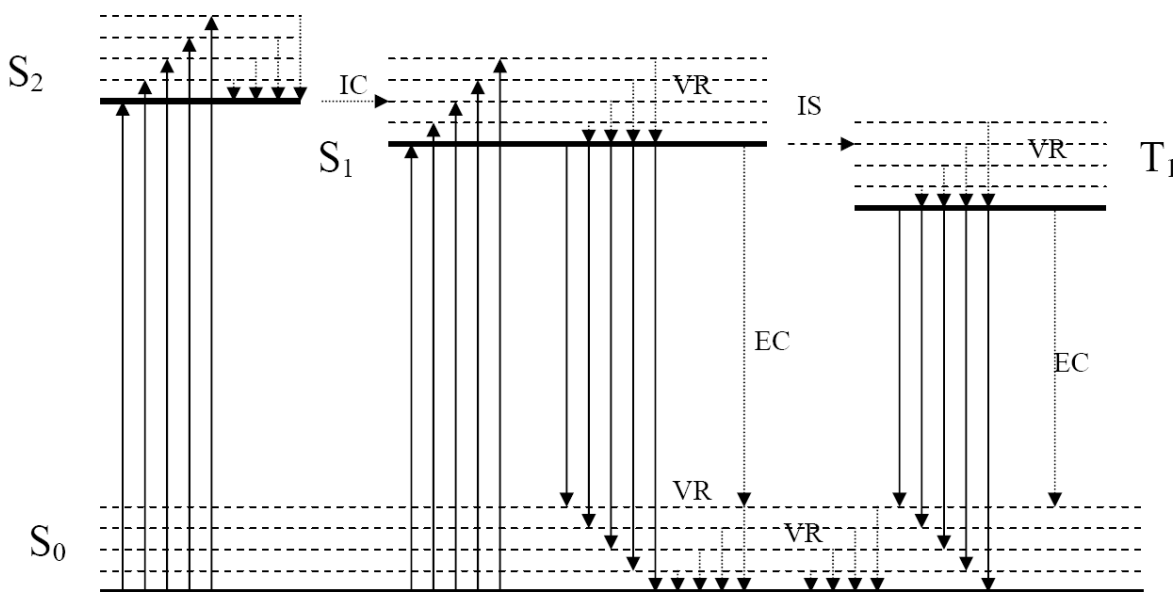
$[\text{Cl}^-] = 2.64 \text{ M}$

4] Sketch a signal-concentration diagram clearly illustrating the concepts of sensitivity, detection limit and back ground. (15 points)



5] (25 points) Draw a Joblonski diagram clearly illustrating the following processes.

- i) absorption
- j) emission
- k) fluorescence
- l) phosphorescence
- m) vibrational relaxation
- n) external conversion
- o) internal conversion
- p) intersystem crossing



6] (5 points) Which of the transitions above are considered radiationless decays?

VR, and EC.

7] (10 points) What is the 95% confidence limit for the following set of data.

4.88, 5.13, 4.92, 5.22, 5.07, 4.72

Avg = 4.99 s.d. = 0.184

$\mu = \bar{x} \pm t_{s/n}^{1/2} = 4.99 \pm 2.571(0.184)/(6)^{1/2}$ $\mu = 4.99 \pm 0.19$

8] The response of a Cl⁻ ISE electrode was a -455 mV in a solution of 4.33e-3 M KCl. An unknown solution gave a potential -474 mV. What is [Cl⁻] of this unknown? (10 points)

$E = \text{const} - 0.0592 \log [\text{Cl}^-]$
 $-0.455 \text{ V} = \text{const} - 0.0592 \log [4.33\text{e-}3]$

$$\text{Const} = 0.595$$

$$-0.474 = -0.595 - 0.0592 \log [\text{Cl}^-]$$

$$[\text{Cl}^-] = 9.04 \times 10^{-3} \text{ M}$$

9] An ASV analysis was conducted on a sample containing cadmium. A 1.00 g sample was dissolved in 100.0 mL of nitric acid. A 50.0 mL aliquot gave an ASV signal of 5.00 μA . On the other 50.0 mL aliquot was added a spike of 10.0 μL of $1.00 \times 10^{-2} \text{ M CdCl}_2$ and gave a signal of 6.00 μA . What is concentration of Cd (AW 112.411 g/mol) in the sample in ppm? (15 points)

$$\text{Conc. of Cd in spiked sample} = 10.0 \times 10^{-6} \text{ L} \times 1.00 \times 10^{-2} \text{ mol/L} \times 1/0.0500 \text{ L} = 2.00 \times 10^{-6} \text{ M}$$

$$\text{Slope} = (6.00 - 5.00 \mu\text{A}) / 2.00 \times 10^{-6} \text{ M} = 5.00 \times 10^5$$

$$y = 5.00 \times 10^5(x) + 5.00$$

$$x\text{-int} = -1.00 \times 10^{-5} \text{ M}$$

$$\text{mass Cd} = 1.00 \times 10^{-5} \text{ mol/L} \times 0.100 \times 112.411 \text{ g/mol} = 1.12 \times 10^{-4} \text{ g Cd}$$

$$\text{ppm Cd} = 1.12 \times 10^{-4} \text{ g} / 1.00 \text{ g} \times 10^6 = 112 \text{ ppm}$$

Exam 2 – Chem 454 – March 9 – 100 total points

1] (20 points) a) Sketch and label the major components of a Michelson interferometer. Include the components necessary to describe an interferogram.
b) What is an interferogram? What are the axes in an interferogram?
c) Sketch an interferogram of a single wavelength source. How far back does the moveable mirror move in order to create an intensity minimum?
d) Sketch an interferogram of a broadband source.

2] (10 points) Draw an IR active and for a Raman active vibrational mode for CO₂.

3] (10 points) You are asked to design an experiment for the gas phase analysis of CO₂ in the atmosphere at sea-level. The typical concentrations are 200-400 ppm (by volume). How would you do this? A diagram would help in the description.

4] (20 points) Describe the Raman transition with a 'Jablonski' type diagram. In that diagram label the Stokes, Anti-Stokes and Rayleigh scatterings. Which correspond to the Raman transition? Why is it necessary to use a laser as the source?

5] (10 points) In terms of a more recent development, which is newer the CCD array or the PMT? What do those acronyms stand for? What are they used for?

6] (10 points) What is environmental noise? What is the major source for it? How can it be minimized?

7] (10 points) Is ICP an absorption, emission, or a fluorescence technique? Explain why it has advantages over flame techniques. How does it achieve these advantages?

8] MTBE was analyzed in a gasoline sample by Raman spectroscopy. The sample itself gave an absorption of 0.577. A 10.0-mL aliquot of the sample was then spiked with 10- μ L of MTBE itself (MW 88.15, BP 55.2 °C, 0.7404 g/mL). The spiked sample gave an absorption of 0.722. What is the concentration of MTBE in the sample?

Exam 3 – Chem 454 – April 20, 2007

Answer to # 12] 135 ppm

1] 20 – points: Write down the van Deemter equation and describe its **three major components**. In this description **draw figures depicting the important features** and concepts of the van Deemter components. Finally **sketch a plot of H vs. u for each component and the total effect**.

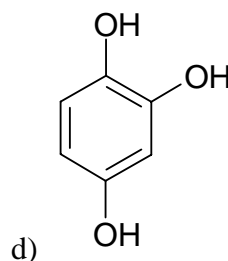
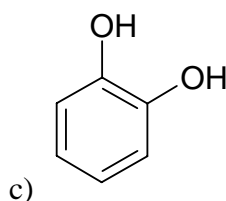
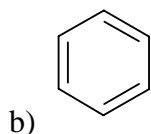
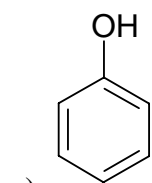
2] 5 – points, How is variance related to plate height? How is plate height related to number of theoretical plates?

4] 15 – points, how does the capillary columns specifically address the three major components of the van Deemter equation?

5] 5 – points, High pressures are required for HPLC because of the small packing particle sizes of the stationary phase supports. Why are diameters of these supports so small?

6] 5 – points, When designing a binary ($\text{CH}_3\text{CN}:\text{H}_2\text{O}$) mobile phase for gradient elution on using a C-18 stationary phase would it be best to increase or decrease the proportion of water during elution? Why?

7] 5- points, Predict the elution order for the following of solutes in normal phase LC:



8] 10 – points, Discuss the relative advantages and disadvantages of two separation columns both with identical features except that one is twice as long as the other.

9] 10 – points, What is the electro-osmotic effect? Sketch a diagram that explains this effect. How does it explain the elution order in capillary electrophoresis?

10] 5 – points, The resolution term in chromatographic separations is proportional to

- (Circle one)
- a. t_r
 - b. k'
 - c. H
 - d. $L^{1/2}$
 - e. $H^{1/2}$

11] 5 – points, The most common mobile phases in GC are

- a. Ar, N₂ and F₂
- b. N₂O, C₂H₂, and O₂
- c. H₂, Ar, and Ne
- d. He, Ne, and Ar
- e. H₂, He, and N₂

12] 15 – points, A GC analysis was conducted on a sample with analyte X. The table below describes the analysis:

Run	X (concentration, peak area, t_r)	IS (concentration, peak area, t_r)
1	112 ppm, 11,202, 6.77 minutes	77.0 ppm, 5,998, 3.44 minutes
2	Unknown, 13,772, 6.67 minutes	77.0 ppm, 6,122, 3.45 minutes

IS is the internal standard. What is the concentration of X in Run 2? Watch Significant Figures.