

Chem 454 – instrumental Analysis – Exam 1 – February 6th, 2008

Name: _____

1] A glass electrode was immersed into a solution of pH 4.33 gave a response of 677.1 mV. This electrode was used to measure a sample solution and gave a response of 544.7 mV. What is the pH of the sample? (15 points)

2] A silver electrode responds with a potential of 0.729 V when 25.00 mL of 0.0400 M KBr solution is mixed with 20.00 mL of 0.200 M AgNO₃(aq). What is the standard reduction potential of Ag⁺? What is the half reaction for that E⁰? (See Homework Problem 22-5c) (15 points) AgBr K_{sp} = 5.0e-13

3] Polarographic analysis of Cd²⁺ yielded a diffusion current of 2.89 μA for a 10.0 mL sample. A spike of 1.00 mL of 0.112 mM added to that sample yielded a diffusion current of 4.32 μA. What is the concentration of Cd²⁺ in the sample? (15 points)

4] Essay Question: What are the diffusion (or faradaic) and the capacitive current s in voltammetry? Emphasize the differences between them, a diagram may be helpful. Which is the signal, and which is the background? (15 points)

5] What is the 90% confidence interval for the following measurements? (15 points)

10.22 11.03 10.71 10.47 10.83

Half Reaction	E ⁰
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	+1.23
$Fe(CN)_6^{3-} + e^- \rightarrow Fe(CN)_6^{4-}$	+0.36
$2H^+ + 2e^- \rightarrow H_2$	0.00
$Pb^{2+} + 2e^- \rightarrow Pb$	-0.126
$PbSO_4 + 2e^- \rightarrow Pb + SO_4^{2-}$	-0.355
$Fe^{2+} + 2e^- \rightarrow Fe$	-0.41

6] Which of the species above is the strongest oxidizing agent? _____ (5 points)

7] Which of the above is the strongest reducing agent? _____ (5 points)

8] From the data in the Table above calculate the K_{sp} of PbSO₄. (15 points)

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Answers

1] A glass electrode was immersed into a solution of pH 4.33 gave a response of 677.1 mV. This electrode was used to measure a sample solution and gave a response of 544.7 mV. What is the pH of the sample? (15 points)

$$E = \text{const} + 0.0592 \log(\text{H}^+) \text{ or } E = \text{const} - 0.0592 \text{ pH}$$

$$0.6771 = \text{const} - 0.0592 (4.33) \quad \text{const} = 0.9333$$

$$0.5447 = 0.9333 - 0.0592 \text{ pH} \quad \text{pH} = 6.56$$

2] A silver electrode responds with a potential of 0.729 V when 25.00 mL of 0.0400 M KBr solution is mixed with 20.00 mL of 0.200 M AgNO₃(aq). What is the standard reduction potential of Ag⁺? What is the half reaction for that E⁰? (See Homework Problem 22-5c) (15 points)

$$\text{AgBr } K_{\text{sp}} = 5.0\text{e-}13$$

$$\text{mmol Br}^- \text{ added} = 25.0 \text{ mL } (0.0400 \text{ M}) = 1.00$$

$$\text{mmol Ag}^+ \text{ added} = 20.0 \text{ mL } (0.200 \text{ M}) = 4.00$$

$$\text{mmol Ag}^+ \text{ left after precipitation} = 4.00 - 1.00 = 3.00$$

$$[\text{Ag}^+] = 3.00 \text{ mmol}/45.0 \text{ mL} = 6.67\text{e-}2$$

$$E = E^0 - 0.0592 \log (\text{Ag}^+)$$

$$0.729 \text{ V} = E^0 - 0.0592 \log 1/(6.67\text{e-}2) \quad E^0 = 0.799 \text{ V} \quad \text{Ag}^+ + \text{e}^- = \text{Ag} \quad E^0 = 0.799 \text{ V}$$

3] Polarographic analysis of Cd²⁺ yielded a diffusion current of 2.89 μA for a 10.0 mL sample. A spike of 1.00 mL of 0.112 mM added to that sample yielded a diffusion current of 4.32 μA. What is the concentration of Cd²⁺ in the sample? (15 points)

$$\text{We know that } i \propto C \text{ Therefore: } i_1/i_2 = C_1/C_2$$

$$\text{let } x = \text{conc } [\text{Cd}^{2+}] \quad 2.89/4.32 = x/((0.112/11) + (10*x/11))$$

$$x = 1.74\text{e-}2 \text{ mM}$$

4] Essay Question: What are the diffusion (or faradaic) and the capacitive currents in voltammetry? Emphasize the differences between them. Which is the signal, and which is the background? (15 points)

5] What is the 90% confidence interval for the following measurements? (15 points)

10.22 11.03 10.71 10.47 10.83

$$\bar{x} = 10.65$$

$$s = \{[(10.22-10.65)^2 + (11.03-10.65)^2 + (10.71-10.65)^2 + (10.47-10.65)^2 + (10.83-10.65)^2]/(5-1)\}^{1/2} = 0.32$$

$$\mu = \bar{x} \pm t_{s/n}^{1/2} = 10.65 \pm 2.132(0.32)/5^{1/2} = 10.65 \pm 0.31$$

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Half Reaction	E^0
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$2H^+ + 2e^- \rightarrow H_2$	0.00
$Pb^{2+} + 2e^- \rightarrow Pb$	-0.126
$PbSO_4 + 2e^- \rightarrow Pb + SO_4^{2-}$	-0.355
$Fe^{2+} + 2e^- \rightarrow Fe$	-0.41

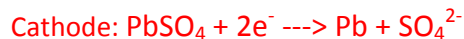
6] Which of the species above is the strongest oxidizing agent? _____ (5 points)

O_2

7] Which of the above is the strongest reducing agent? _____ (5 points)

Fe

8] From the data in the Table above calculate the K_{sp} of $PbSO_4$. (15 points)



$$E^0 = -0.355 + 0.126 = -0.229 \text{ V}$$

$$\Delta G = -nFE = -RT \ln K$$

$$E^0 = 0.0592/n \log K$$

$$-0.229 = 0.0592/2 \log K_{sp} \quad K_{sp} = 1.8e-8$$

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

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

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$ 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

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The Periodic Table of the Elements

1	2																																																																																																																																																																																																																																																																																																																																																																																																													
H Hydrogen 1.00794	He Helium 4.003																																																																																																																																																																																																																																																																																																																																																																																																													
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Li Lithium 6.941	Be Beryllium 9.012182	B Boron 10.811	C Carbon 12.0107	N Nitrogen 14.00674	O Oxygen 15.9994	F Fluorine 18.9984032	Ne Neon 20.1797																																																																																																																																																																																																																																																																																																																																																																																																							
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Na Sodium 22.989770	Mg Magnesium 24.3050	Al Aluminum 26.981538	Si Silicon 28.0855	P Phosphorus 30.973761	S Sulfur 32.066	Cl Chlorine 35.4527	Ar Argon 39.948																																																																																																																																																																																																																																																																																																																																																																																																							
19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36																																																																																																																																																																																																																																																																																																																																																																																													
K Potassium 39.0983	Ca Calcium 40.078	Sc Scandium 44.955910	Ti Titanium 47.867	V Vanadium 50.9415	Cr Chromium 51.9961	Mn Manganese 54.938049	Fe Iron 55.845	Co Cobalt 58.933200	Ni Nickel 58.6934	Cu Copper 63.546	Zn Zinc 65.39	Ga Gallium 69.723	Ge Germanium 72.61	As Arsenic 74.92160	Se Selenium 78.96	Br Bromine 79.904	Kr Krypton 83.80																																																																																																																																																																																																																																																																																																																																																																																													
37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54																																																																																																																																																																																																																																																																																																																																																																																													
Rb Rubidium 85.4678	Sr Strontium 87.62	Y Yttrium 88.90585	Zr Zirconium 91.224	Nb Niobium 92.90638	Mo Molybdenum 95.94	Tc Technetium (98)	Ru Ruthenium 101.07	Rh Rhodium 102.90550	Pd Palladium 106.42	Ag Silver 107.8682	Cd Cadmium 112.411	In Indium 114.818	Sn Tin 118.710	Sb Antimony 121.760	Te Tellurium 127.60	I Iodine 126.90447	Xe Xenon 131.29																																																																																																																																																																																																																																																																																																																																																																																													
55	56	57	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86																																																																																																																																																																																																																																																																																																																																																																																													
Cs Cesium 132.90545	Ba Barium 137.327	La Lanthanum 138.9055	Hf Hafnium 178.49	Ta Tantalum 180.9479	W Tungsten 183.84	Re Rhenium 186.207	Os Osmium 190.23	Ir Iridium 192.217	Pt Platinum 195.078	Au Gold 196.96655	Hg Mercury 200.59	Tl Thallium 204.3833	Pb Lead 207.2	Bi Bismuth 208.98038	Po Polonium (209)	At Astatine (210)	Rn Radon (222)																																																																																																																																																																																																																																																																																																																																																																																													
87	88	89	104	105	106	107	108	109	110	111	112	113	114																																																																																																																																																																																																																																																																																																																																																																																																	
Fr Francium (223)	Ra Radium (226)	Ac Actinium (227)	Rf Rutherfordium (261)	Db Dubnium (262)	Sg Seaborgium (263)	Bh Bohrium (262)	Hs Hassium (265)	Mt Meitnerium (266)	Pt Platinum (269)	Cu Copper (272)	Zn Zinc (277)	In Indium (283)	Sn Tin (286)	Pb Lead (282)	Bi Bismuth (284)	Po Polonium (286)	At Astatine (285)	Rn Radon (286)																																																																																																																																																																																																																																																																																																																																																																																												
89	90	91	92	93	94	95	96	97	98	99	100	101	102	103																																																																																																																																																																																																																																																																																																																																																																																																
Th Thorium 232.0381	Pa Protactinium 231.03588	U Uranium 238.0289	Np Neptunium (237)	Pu Plutonium (244)	Am Americium (243)	Cm Curium (247)	Bk Berkelium (247)	Cf Californium (251)	Es Einsteinium (252)	Fm Fermium (257)	Md Mendelevium (258)	No Nobelium (259)	Lr Lawrencium (262)	Rf Rutherfordium (261)	Db Dubnium (262)	Sg Seaborgium (263)	Bh Bohrium (262)	Hs Hassium (265)	Mt Meitnerium (266)	Pt Platinum (269)	Cu Copper (272)	Zn Zinc (277)	In Indium (283)	Sn Tin (286)	Pb Lead (282)	Bi Bismuth (284)	Po Polonium (286)	At Astatine (285)	Rn Radon (286)	Fr Francium (223)	Ra Radium (226)	Ac Actinium (227)	Rf Rutherfordium (261)	Db Dubnium (262)	Sg Seaborgium (263)	Bh Bohrium (262)	Hs Hassium (265)	Mt Meitnerium (266)	Pt Platinum (269)	Cu Copper (272)	Zn Zinc (277)	In Indium (283)	Sn Tin (286)	Pb Lead (282)	Bi Bismuth (284)	Po Polonium (286)	At Astatine (285)	Rn Radon (286)	Fr Francium (223)	Ra Radium (226)	Ac Actinium (227)	Rf Rutherfordium (261)	Db Dubnium (262)	Sg Seaborgium (263)	Bh Bohrium (262)	Hs Hassium (265)	Mt Meitnerium (266)	Pt Platinum (269)	Cu Copper (272)	Zn Zinc (277)	In Indium (283)	Sn Tin (286)	Pb Lead (282)	Bi Bismuth (284)	Po Polonium (286)	At Astatine (285)	Rn Radon (286)	Fr Francium (223)	Ra Radium (226)	Ac Actinium (227)	Rf Rutherfordium (261)	Db Dubnium (262)	Sg Seaborgium (263)	Bh Bohrium (262)	Hs Hassium (265)	Mt Meitnerium (266)	Pt Platinum (269)	Cu Copper (272)	Zn Zinc (277)	In Indium (283)	Sn Tin (286)	Pb Lead (282)	Bi Bismuth (284)	Po Polonium (286)	At Astatine (285)	Rn Radon (286)	Fr Francium (223)	Ra Radium (226)	Ac Actinium (227)	Rf Rutherfordium (261)	Db Dubnium (262)	Sg Seaborgium (263)	Bh Bohrium (262)	Hs Hassium (265)	Mt Meitnerium (266)	Pt Platinum (269)	Cu Copper (272)	Zn Zinc (277)	In Indium (283)	Sn Tin (286)	Pb Lead (282)	Bi Bismuth (284)	Po Polonium (286)	At Astatine (285)	Rn Radon (286)	Fr Francium (223)	Ra Radium (226)	Ac Actinium (227)	Rf Rutherfordium (261)	Db Dubnium (262)	Sg Seaborgium (263)	Bh Bohrium (262)	Hs Hassium (265)	Mt Meitnerium (266)	Pt Platinum (269)	Cu Copper (272)	Zn Zinc (277)	In Indium (283)	Sn Tin (286)	Pb Lead (282)	Bi Bismuth (284)	Po Polonium (286)	At Astatine (285)	Rn Radon (286)	Fr Francium (223)	Ra Radium (226)	Ac Actinium (227)	Rf Rutherfordium (261)	Db Dubnium (262)	Sg Seaborgium (263)	Bh Bohrium (262)	Hs Hassium (265)	Mt Meitnerium (266)	Pt Platinum (269)	Cu Copper (272)	Zn Zinc (277)	In Indium (283)	Sn Tin (286)	Pb Lead (282)	Bi Bismuth (284)	Po Polonium (286)	At Astatine (285)	Rn Radon (286)	Fr Francium (223)	Ra Radium (226)	Ac Actinium (227)	Rf Rutherfordium (261)	Db Dubnium (262)	Sg Seaborgium (263)	Bh Bohrium (262)	Hs Hassium (265)	Mt Meitnerium (266)	Pt Platinum (269)	Cu Copper (272)	Zn Zinc (277)	In Indium (283)	Sn Tin (286)	Pb Lead (282)	Bi Bismuth (284)	Po Polonium (286)	At Astatine (285)	Rn Radon (286)	Fr Francium (223)	Ra Radium (226)	Ac Actinium (227)	Rf Rutherfordium (261)	Db Dubnium (262)	Sg Seaborgium (263)	Bh Bohrium (262)	Hs Hassium (265)	Mt Meitnerium (266)	Pt Platinum (269)	Cu Copper (272)	Zn Zinc (277)	In Indium (283)	Sn Tin (286)	Pb Lead (282)	Bi Bismuth (284)	Po Polonium (286)	At Astatine (285)	Rn Radon (286)	Fr Francium (223)	Ra Radium (226)	Ac Actinium (227)	Rf Rutherfordium (261)	Db Dubnium (262)	Sg Seaborgium (263)	Bh Bohrium (262)	Hs Hassium (265)	Mt Meitnerium (266)	Pt Platinum (269)	Cu Copper (272)	Zn Zinc (277)	In Indium (283)	Sn Tin (286)	Pb Lead (282)	Bi Bismuth (284)	Po Polonium (286)	At Astatine (285)	Rn Radon (286)	Fr Francium (223)	Ra Radium (226)	Ac Actinium (227)	Rf Rutherfordium (261)	Db Dubnium (262)	Sg Seaborgium (263)	Bh Bohrium (262)	Hs Hassium (265)	Mt Meitnerium (266)	Pt Platinum (269)	Cu Copper (272)	Zn Zinc (277)	In Indium (283)	Sn Tin (286)	Pb Lead (282)	Bi Bismuth (284)	Po Polonium (286)	At Astatine (285)	Rn Radon (286)	Fr Francium (223)	Ra Radium (226)	Ac Actinium (227)	Rf Rutherfordium (261)	Db Dubnium (262)	Sg Seaborgium (263)	Bh Bohrium (262)	Hs Hassium (265)	Mt Meitnerium (266)	Pt Platinum (269)	Cu Copper (272)	Zn Zinc (277)	In Indium (283)	Sn Tin (286)	Pb Lead (282)	Bi Bismuth (284)	Po Polonium (286)	At Astatine (285)	Rn Radon (286)	Fr Francium (223)	Ra Radium (226)	Ac Actinium (227)	Rf Rutherfordium (261)	Db Dubnium (262)	Sg Seaborgium (263)	Bh Bohrium (262)	Hs Hassium (265)	Mt Meitnerium (266)	Pt Platinum (269)	Cu Copper (272)	Zn Zinc (277)	In Indium (283)	Sn Tin (286)	Pb Lead (282)	Bi Bismuth (284)	Po Polonium (286)	At Astatine (285)	Rn Radon (286)	Fr Francium (223)	Ra Radium (226)	Ac Actinium (227)	Rf Rutherfordium (261)	Db Dubnium (262)	Sg Seaborgium (263)	Bh Bohrium (262)	Hs Hassium (265)	Mt Meitnerium (266)	Pt Platinum (269)	Cu Copper (272)	Zn Zinc (277)	In Indium (283)	Sn Tin (286)	Pb Lead (282)	Bi Bismuth (284)	Po Polonium (286)	At Astatine (285)	Rn Radon (286)	Fr Francium (223)	Ra Radium (226)	Ac Actinium (227)	Rf Rutherfordium (261)	Db Dubnium (262)	Sg Seaborgium (263)	Bh Bohrium (262)	Hs Hassium (265)	Mt Meitnerium (266)	Pt Platinum (269)	Cu Copper (272)	Zn Zinc (277)	In Indium (283)	Sn Tin (286)	Pb Lead (282)	Bi Bismuth (284)	Po Polonium (286)	At Astatine (285)	Rn Radon (286)	Fr Francium (223)	Ra Radium (226)	Ac Actinium (227)	Rf Rutherfordium (261)	Db Dubnium (262)	Sg Seaborgium (263)	Bh Bohrium (262)	Hs Hassium (265)	Mt Meitnerium (266)	Pt Platinum (269)	Cu Copper (272)	Zn Zinc (277)	In Indium (283)	Sn Tin (286)	Pb Lead (282)	Bi Bismuth (284)	Po Polonium (286)	At Astatine (285)	Rn Radon (286)	Fr Francium (223)	Ra Radium (226)	Ac Actinium (227)	Rf Rutherfordium (261)	Db Dubnium (262)	Sg Seaborgium (263)	Bh Bohrium (262)	Hs Hassium (265)	Mt Meitnerium (266)	Pt Platinum (269)	Cu Copper (272)	Zn Zinc (277)	In Indium (283)	Sn Tin (286)	Pb Lead (282)	Bi Bismuth (284)	Po Polonium (286)	At Astatine (285)	Rn Radon (286)	Fr Francium (223)	Ra Radium (226)	Ac Actinium (227)	Rf Rutherfordium (261)	Db Dubnium (262)	Sg Seaborgium (263)	Bh Bohrium (262)	Hs Hassium (265)	Mt Meitnerium (266)	Pt Platinum (269)	Cu Copper (272)	Zn Zinc (277)	In Indium (283)	Sn Tin (286)	Pb Lead (282)	Bi Bismuth (284)	Po Polonium (286)	At Astatine (285)	Rn Radon (286)	Fr Francium (223)	Ra Radium (226)	Ac Actinium (227)	Rf Rutherfordium (261)	Db Dubnium (262)	Sg Seaborgium (263)	Bh Bohrium (262)	Hs Hassium (265)	Mt Meitnerium (266)	Pt Platinum (269)	Cu Copper (272)	Zn Zinc (277)	In Indium (283)	Sn Tin (286)	Pb Lead (282)	Bi Bismuth (284)	Po Polonium (286)	At Astatine (285)	Rn Radon (286)	Fr Francium (223)	Ra Radium (226)	Ac Actinium (227)	Rf Rutherfordium (261)	Db Dubnium (262)	Sg Seaborgium (263)	Bh Bohrium (262)	Hs Hassium (265)	Mt Meitnerium (266)	Pt Platinum (269)	Cu Copper (272)	Zn Zinc (277)	In Indium (283)	Sn Tin (286)	Pb Lead (282)	Bi Bismuth (284)	Po Polonium (286)	At Astatine (285)	Rn Radon (286)	Fr Francium (223)	Ra Radium (226)	Ac Actinium (227)	Rf Rutherfordium (261)	Db Dubnium (262)	Sg Seaborgium (263)	Bh Bohrium (262)	Hs Hassium (265)

Chem 454 – instrumental Analysis – Exam 2 – March 5, 2008

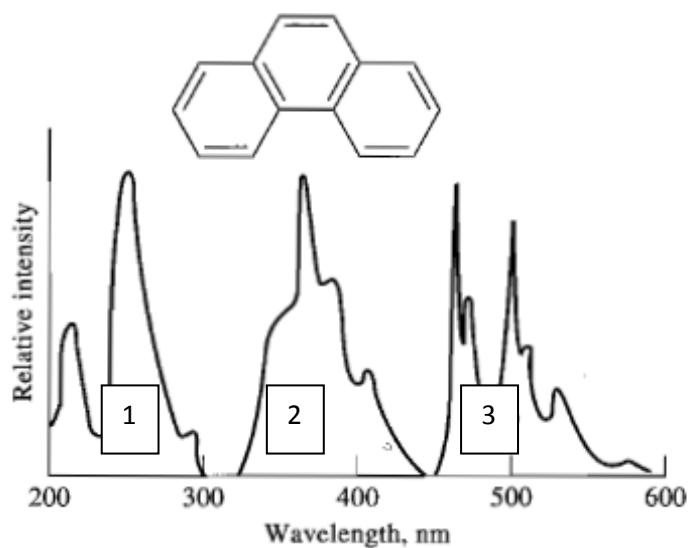
You may keep these questions after the exam. Please record your name on the Scantron sheet and turn it in when you are finished.

1] Raman Active stretches are a result of changes in:

- Redox potential
- Dipole Moment
- Polarization
- Intersystem Crossing
- Overpotentials

2] Spectral absorbances in the near-IR region are a result of

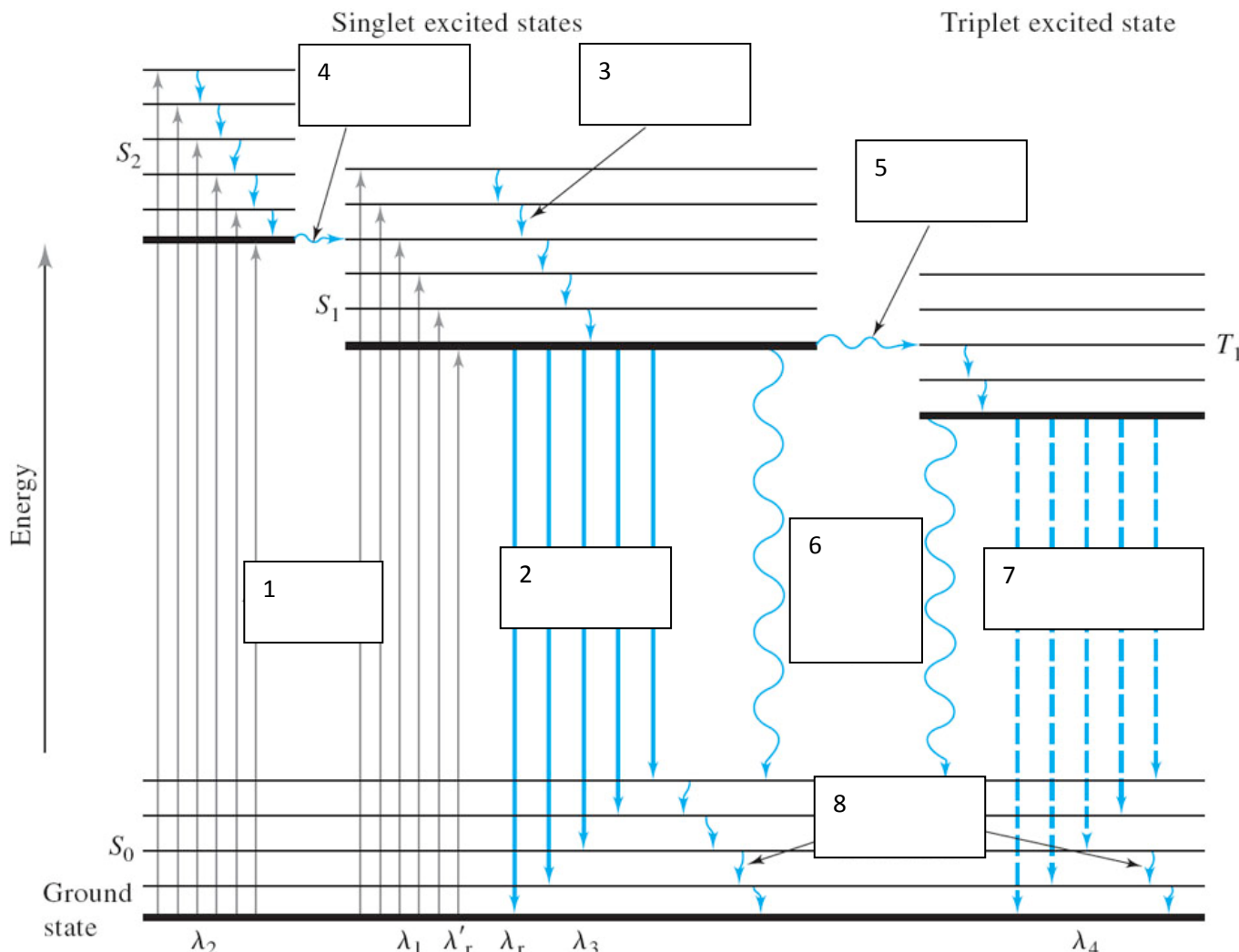
- $\Delta v = 1$
- $\Delta v > 1$
- $\Delta v < 1$
- $\Delta v = 0$
- $\Delta v = -1$



F = fluorescence; P = phosphorescence; E = excitation

3] In the diagram taken from your text (above) the three labeled regions represent

- 1-F, 2-P, 3-E
- 1-P, 2-E, 3-F
- 1-E, 2-P, 3-F
- 1-P, 2-F, 3-E
- 1-E, 2-F, 3-P



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Questions 4-8 regard the figure above

4) In the diagram above which of the following represent vibrational relaxations?

- a) 5
- b) 7
- c) 1
- d) 8
- e) 4

5) Which of the following represent an absorbance?

- a) 1
- b) 2
- c) 3
- d) 4
- e) 5

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6] Which of following represents an emission?

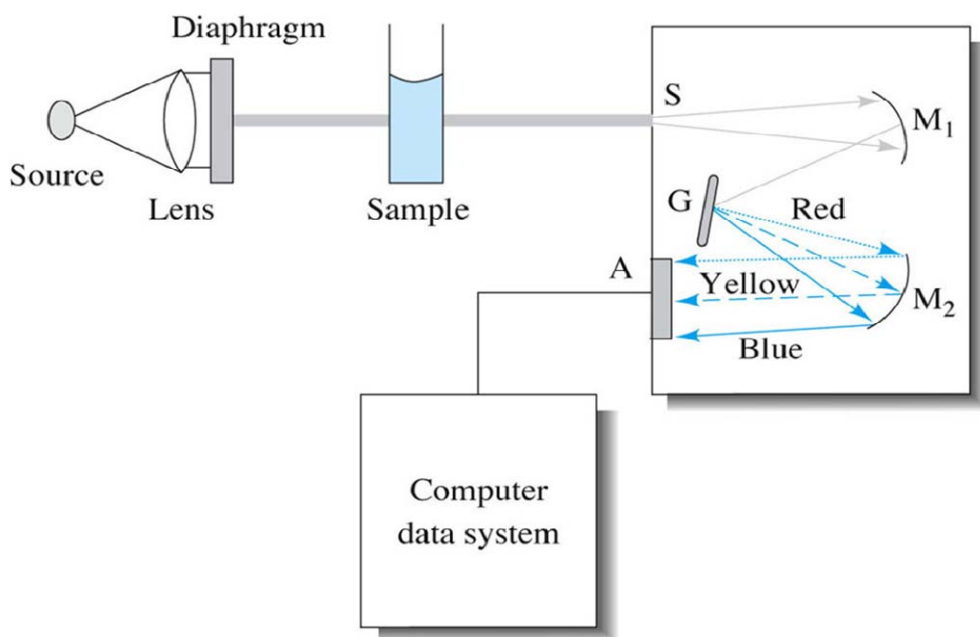
- a) 1
- b) 2
- c) 3
- d) 4
- e) 5

7] Which of the following is an intersystem crossing?

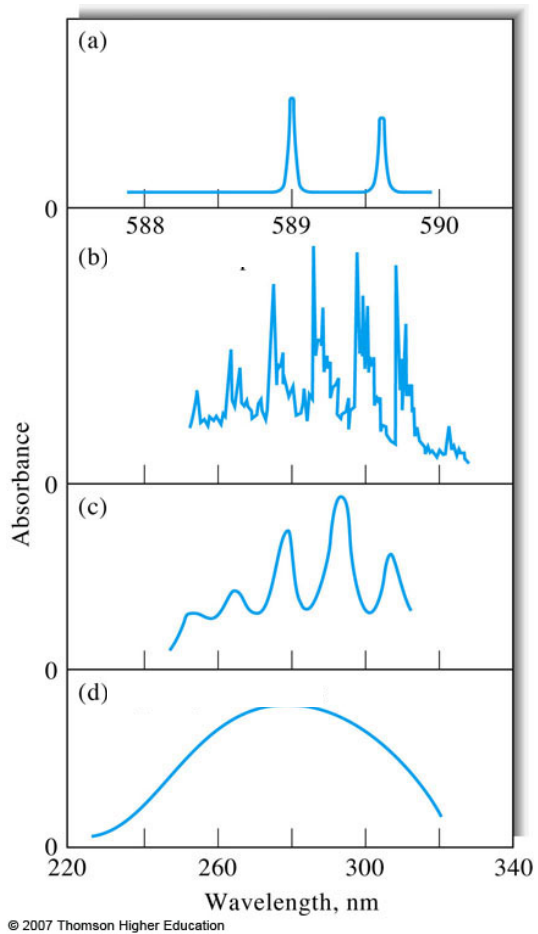
- a) 2
- b) 1
- c) 8
- d) 5
- e) 4

8] Which of the following is a forbidden electronic state transition?

- a) $S_2 \rightarrow S_1$
- b) $S_0 \rightarrow S_1$
- c) $S_1 \rightarrow S_0$
- d) $T_1 \rightarrow S_0$
- e) None of the above



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Questions 14-17 are based on the diagram above. If needed ask the proctor to draw benzene and biphenyl on the chalk board.

14] Which of spectra is most likely Na vapor?

- a)
- b)
- c)
- d)

15] Which is most likely biphenyl in hexane?

- a)
- b)
- c)
- d)

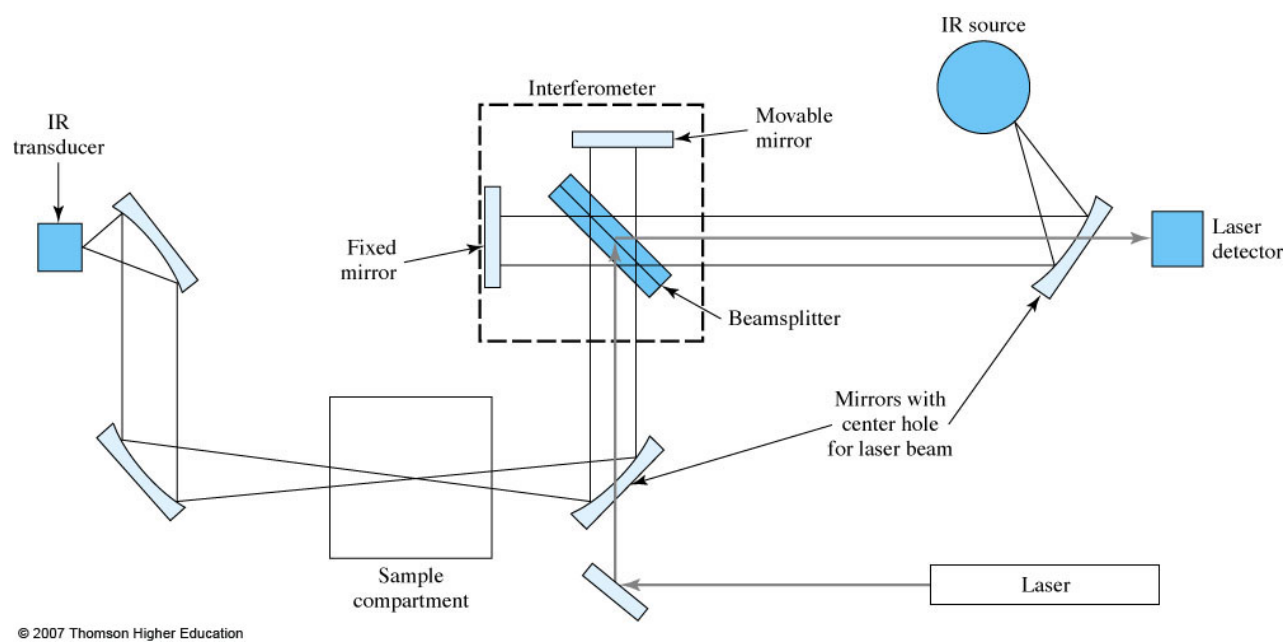
Chem 454 – instrumental Analysis – Exam 2 – March 5, 2008

16] Which is most likely benzene in hexane?

- a)
- b)
- c)
- d)

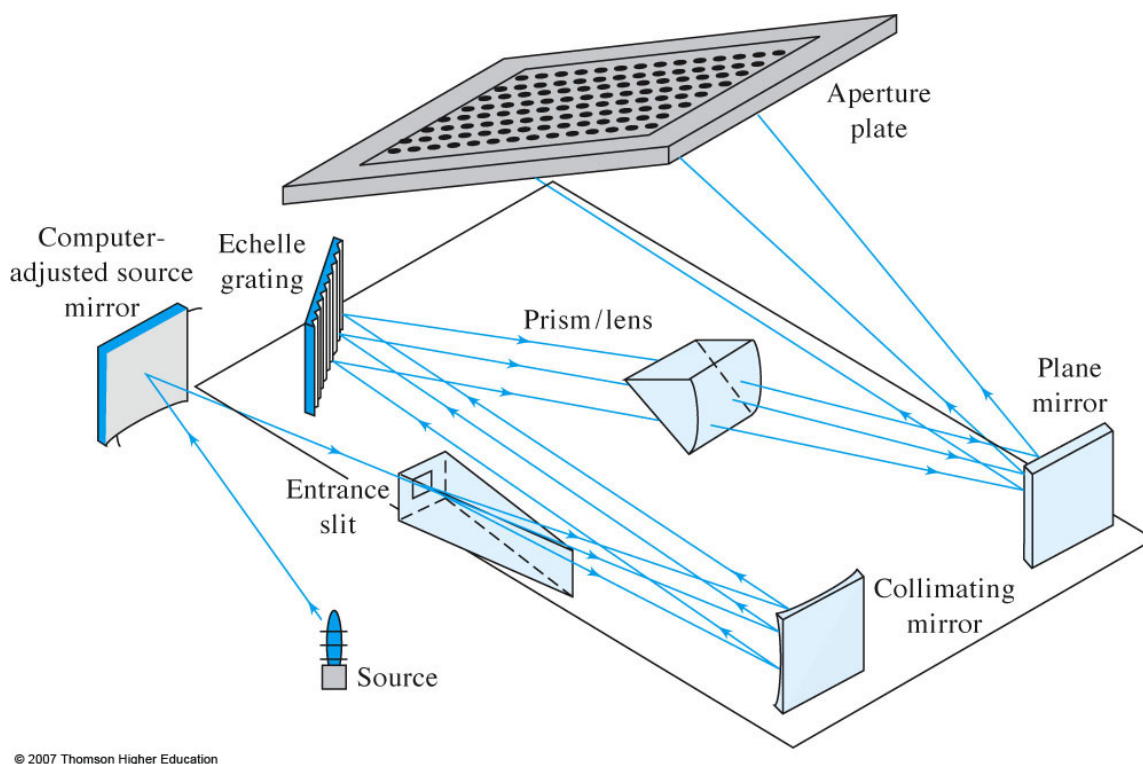
17] Which is most likely benzene vapor?

- a)
- b)
- c)
- d)



18] The diagram above is a representation of

- a) UV-vis absorbance spectrophotometer
- b) Scanning IR
- c) FT-IR
- d) Fluorometer
- e) monochrometer



19] The diagram above is a representation of a

- a) FT-IR
- b) CCD spectrometer
- c) PDA spectrometer
- d) Scanning IR
- e) Scanning UV-vis spectrophotometer

20] A Beer's law measurement was made at 355 nm on a 9.00 mL sample with analyte X. Its absorbance A , was found to be 0.200. A spike of 1.0 mL of 1.00 mM compound X was made on that sample and A was found to be 0.250. What is the concentration of X in the sample?

- a) 5.00 mM
- b) 1.00 mM
- c) 0.500 mM
- d) 0.286 mM
- e) 0.132 mM

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Exam 2 Answers

1. C
2. B
3. E
4. D
5. A
6. 2
7. D
8. D
9. B
10. A
11. C
12. D
13. D
14. A
15. D
16. C
17. B
18. C
19. B
20. D

$$0.200/0.250 = x/\{(1/10)1.00 + (9/10)x\}$$

$$X = 0.286 \text{ mM}$$

Name: _____

10 questions @10 points each

1] Describe chemical ionization in mass spectrometry. What type of information is it likely to give about the analyte?

2] What is the electro-osmotic effect in capillary electrophoresis? Why do all species migrate to one electrode? Do they migrate to the cathode or the anode? What is the general order of migration time for cations, anions, and neutrals? Why are neutrals poorly resolved?

3] When considering the van Deemter equation, why does HPLC require small column packing particles?

4] What is gradient elution and how does this differ from an isocratic one? What advantage does gradient elution have over isocratic separations? When using a C-18 stationary phase is it more beneficial to increase or decrease m.p. ~~composition~~ polarity during elution?

5] What is meant by a bulk property detector? Give an example of an HPLC detector that is based on bulk properties and one that is not.

6] Why do capillary columns predominate in analytical GC?

7] What is temperature programming in GC? How does it gain an advantage over single T separations?

8] What is the electron capture detector? Explain its basis for operation, why is N₂ necessary? What types of species are detected with the ECD?

9] Generally, it is thought by many chromatography dilettantes that twice the column length will give you twice the separation "power". Comment on why this is false.

10] A GC-FID analysis was conducted on a soil sample containing pollutant X. The following separations were conducted:

		t _r (minutes)	peak area
Injection 1	21.1 ppm Toluene Internal Standard	10.11	36,242
	33.4 ppm X	14.82	45,997
Injection 2	21.1 ppm Toluene Internal Standard	10.05	38,774
	unknown concentration X	14.77	39,115

What is the concentration of X in the sample?

ANSWERS

1] Describe chemical ionization in mass spectrometry. What type of information is it likely to give about the analyte?

See for example: http://en.wikipedia.org/wiki/Chemical_ionization

2] What is the electro-osmotic effect in capillary electrophoresis? Why do all species migrate to one electrode? Do they migrate to the cathode or the anode? What is the general order of migration time for cations, anions, and neutrals? Why are neutrals poorly resolved?

http://en.wikipedia.org/wiki/Capillary_electrophoresis

3] When considering the van Deemter equation, why does HPLC require small column packing particles?

$$H = A + B/u + Cu$$

In the v-D equation the MT effects predominate, i.e. Cu. Increasing the surface area/bulk ratio of the s.p. is a way to greatly improve the MT between the two phases. This requires small diameter supports for the s.p. The cost is the pressure required to squeeze the m.p. through the space between the smaller diameter particles.

4] What is gradient elution and how does this differ from an isocratic one? What advantage does gradient elution have over isocratic separations? When using a C-18 stationary phase is it more beneficial to increase or decrease m.p. polarity during elution?

Gradient elutions vary the m.p. solvent composition and polarity during separation. This has an advantage over isocratic separations where solvent compositions are kept constant. A gradient elution will allow for the separation of a large variety of species with a broad spectrum of polarities with a much shorter time than isocratic ones. Generally it's best that polarity decrease during separation when using a C-18 s.p. If a non-polar m.p. is used at the beginning of the elution, there will be no retention between the solutes and the C-18 s.p.

5] What is meant by a bulk property detector? Give an example of an HPLC detector that is based on bulk properties and one that is not.

See problem 28-7 h. Measure a physical property of the m.p. Example – UV-vis absorbance, fluorescence techniques are examples of bulk property detectors. Electrochemical detectors are not, since they are based on redox exchanges with solutes near the electrode surface.

6] Why do capillary columns predominate in analytical GC?

Again this gets back to the v-D eqn. The B/u, longitudinal diffusion term contributes most to band broadening in the gas phase. Capillary columns allow for the unobstructed and therefore faster flow of the gaseous m.p. over their packed counterparts.

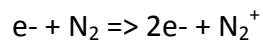
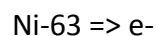
7] What is temperature programming in GC? How does it gain an advantage over single T separations?

By going from colder to warmer temperatures, it is possible to add another dimension separation of solutes beyond the chromatographic ones. This is based on boiling point differences. Generally the initial T is below that of the solutes species and slowly ramped up. See also problem 27-3.

8] What is the electron capture detector? Explain its basis for operation, why is N₂ necessary? What types of species are detected with the ECD?

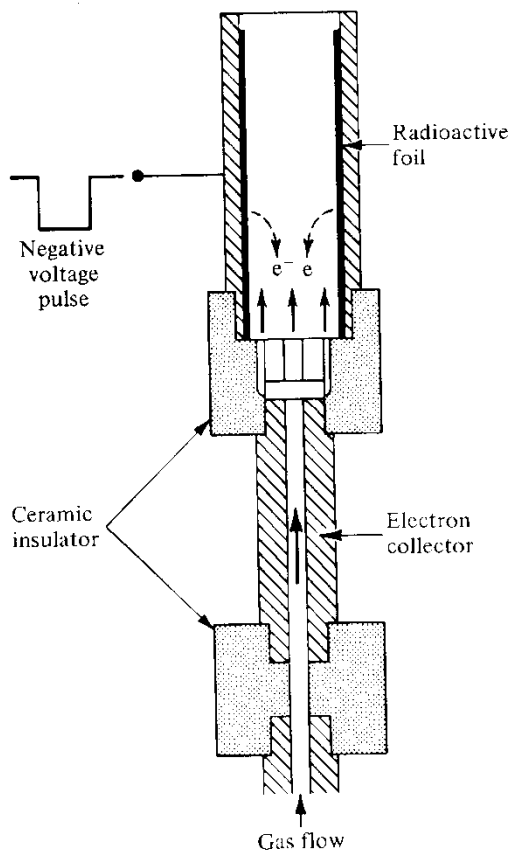
See <http://www.instrumentalchemistry.com/gasphase/pages/e.cd.htm>

Nickel-63 source emits energetic electrons collides with N₂ (introduced as make-up gas or can be used as carrier gas) producing more electrons:

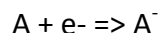


The result is a constant current that is detected by the electron collector (anode).

FIGURE 18.10
Electron capture detector. (Courtesy of Varian Associates.)



As an analyte flows through past the Ni-63 source electron capture is possible by electron-withdrawing species:



Current decreases as a result of e⁻ capture by analyte. This is one of the few instances in which a signal is produced by a decrease in detectable phenomenon.

Sensitive to electron withdrawing groups especially towards organics containing -F, -Cl, -Br, -I also, -CN, NO₂

9] Generally, it is thought by many chromatography dilettantes that twice the column length will give you twice the separation "power". Comment on why this is false.

Remember that $R_s \propto L^{1/2}$. See chapter 26 pages 776-782. So 2x the column length increase resolution by 1.4. Also remember that B/u effects increase with separation time and 2x will increase t by 2x. Also, using a longer column uses more m.p. and decreases experimental throughput.

10] A GC-FID analysis was conducted on a soil sample containing pollutant X. The following separations were conducted:

		t _r (minutes)	peak area
Injection 1	21.1 ppm Toluene Internal Standard	10.11	36,242
	33.4 ppm X	14.82	45,997
Injection 2	21.1 ppm Toluene Internal Standard	10.05	38,774
	unknown concentration X	14.77	39,115

What is the concentration of X in the sample?

$$39,115 * (36,242 / 39,115) * (33.4 \text{ ppm} / 45,997) = 26.3 \text{ ppm}$$