Equation 1: $\bar{x} = \frac{\sum_i x_i}{n}$

Equation 2: $s = \sqrt{\frac{\sum_i \left(x_i - \bar{x}\right)^2}{n-1}}$

Equation 3: $\mu = \bar{x} \pm \frac{t\sigma}{\sqrt{n}}$

Equation 4: $Q = \frac{d}{w}$

Equation 5: $G = \frac{|value - \bar{x}|}{s}$

Values of Grubbs Statistic (G)

Number of Observations n	Confidence Level (%) 99.9	99.5	99	97.5	95	90
3	1.155	1.155	1.155	1.155	1.153	1.148
4	1.499	1.496	1.492	1.481	1.463	1.425
5	1.780	1.764	1.749	1.715	1.672	1.602
6	2.011	1.973	1.944	1.887	1.822	1.729
7	2.201	2.139	2.097	2.020	1.938	1.828
8	2.358	2.274	2.221	2.126	2.032	1.909
9	2.492	2.387	2.323	2.215	2.110	1.977
10	2.606	2.482	2.410	2.290	2.176	2.036
11	2.705	2.564	2.485	2.355	2.234	2.088
12	2.791	2.636	2.550	2.412	2.285	2.134
13	2.867	2.699	2.607	2.462	2.331	2.175
14	2.935	2.755	2.659	2.507	2.371	2.213
15	2.997	2.806	2.705	2.549	2.409	2.247

Equation 6: $F = \frac{s_1^2}{s_2^2}$

Equation 7: $t_{calculated} = \frac{|\bar{x}_1 - \bar{x}_2|}{s_{pooled}} \sqrt{\frac{n_1 n_2}{n_1 + n_2}}$

Equation 8: d.f. = $n_1 + n_2 - 2$

Equation 9: $t_{calculated} = \frac{|\bar{x}_1 - \bar{x}_2|}{\sqrt{\frac{s_1^2}{n_1} + \frac{s_2^2}{n_2}}}$

Equation 10: d.f. = $\left(\frac{\left(\frac{s_1^2}{n_1} + \frac{s_2^2}{n_2}\right)^2}{\frac{(s_1^2/n_1)^2}{n_1+1} + \frac{(s_2^2/n_2)^2}{n_2+1}} \right) - 2$

Equation 11: $E_{cell} = E_{cell}^0 - \frac{RT}{nF} \ln \frac{[\mathrm{Re}d]}{[Ox]}$

Table 4-1 Ordinate and area for the normal (Gaussian) error curve, $y = \frac{1}{\sqrt{2\pi}} e^{-z^2/2}$

$\lvert z\rvert$[a]	y	Area[b]	$\lvert z\rvert$	y	Area	$\lvert z\rvert$	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

	Confidence level (%)						
Degrees of freedom	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

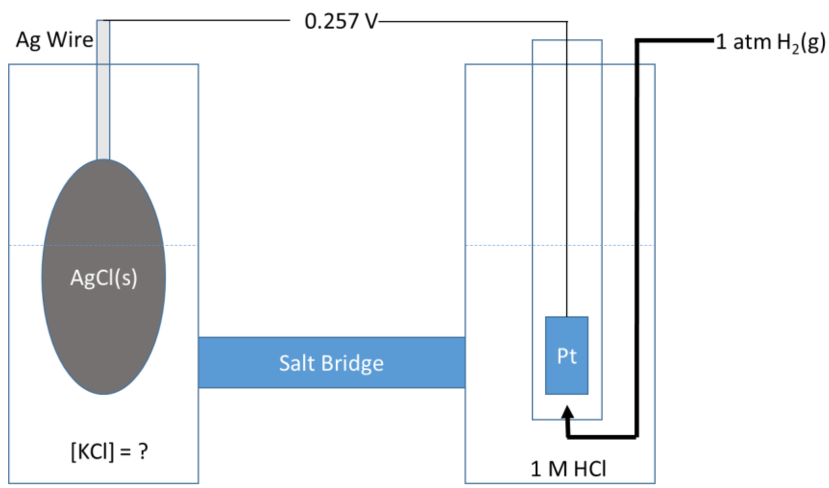
Degrees of freedom for s_2	Degrees of freedom for s_1													
	2	3	4	5	6	7	8	9	10	12	15	20	30	∞
2	19.0	19.2	19.2	19.3	19.3	19.4	19.4	19.4	19.4	19.4	19.4	19.4	19.5	19.5
3	9.55	9.28	9.12	9.01	8.94	8.89	8.84	8.81	8.79	8.74	8.70	8.66	8.62	8.53
4	6.94	6.59	6.39	6.26	6.16	6.09	6.04	6.00	5.96	5.91	5.86	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, 2018

Name____

1] The linear range of a glass pH electrode is pH =______________ to pH =_____________.[1]

2] The potential of the Ag/AgCl electrode is 0.0.257 volts vs. S.H.E in the cell below.



Given the standard reduction potential: $AgCl(s) + e^- \rightarrow Ag(s) + Cl^-$ $E^0 = 0.222$ V

Calculate the concentration of KCl in this electrode.[2]

3) Sketch the configuration of a modern commercial pH/reference electrode configuration.[3]

4] Which of the equations on the formula sheet would best describe precision? [4]

5] The Pb content of a clay was determined. The following results are reported in ppm.

19.941 19.812 19.829 19.828 19.742
19.797 19.937 19.847 19.885 19.804

The mean is 19.842 ppm with s = 0.0627 ppm.

Report the 95% confidence interval for that mean. [5]

6] Which of the following samples would be suitable for analysis by a calibration curve technique using a potentiometric device? Which would require a standard addition type of analysis in all likelihood? [6]

a) Ca^{2+} in milk b) Cu^{2+} in distilled water c) Cl^- in blood d) F^- in tooth paste

7] 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? [7]

8] Fluoride concentration was determined with an ISE. A 5.00-mL aliquot of sample was diluted to 10.00-mL with doubly distilled water. The F^- ISE response was measured as -255 mV. To another 5.00-mL aliquot of sample was added 5.00-mL of 1.66e-3 M NaF solution. Its ISE response was measured as -301 mV. What is the concentration of F^- in the sample? [8]

9] Sketch the Gaussian curves that describe the limits of detection. Be sure to include enough information that makes clear the concept of LOD. What is the simple formula that allows you to calculate the LOD? [9]

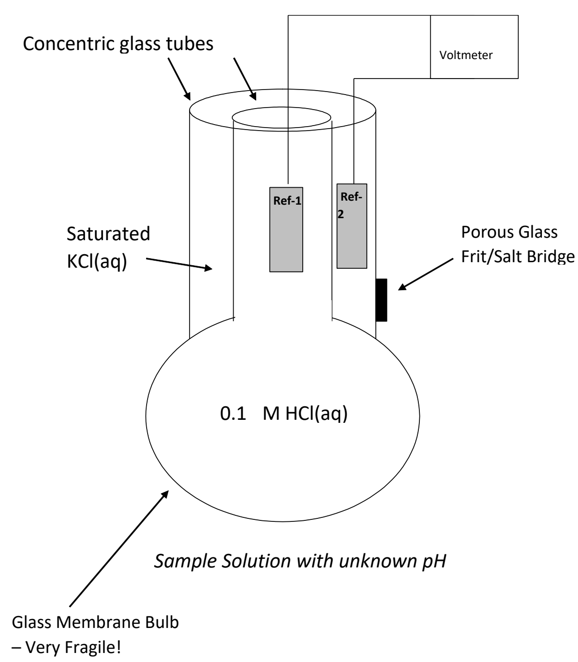
Answers

---

[1] about pH = 2 to pH = 10

[2] $E = 0.222 – 0.0592 \log [Cl^-] = 0.257$ $[Cl^-] = 0.256$ M

[3]



[4] Standard deviation, Equation 2

[5] $\mu = \bar{x} \pm \frac{t\sigma}{\sqrt{n}}$ u = 19.842 ± 2.262 (0.0627/√10) = 19.842 ± 0.0448

There is a 95% chance that true mean lies between 19.797 and 19.887

[6] There can be several ways of answering this question. I will evaluate each based on what you write in your essay. Most likely a), c) and possibly d) will require standard addition type analyses. There is little likelihood of obtaining zero-concentration analyte samples of a) and c). It might be possible to obtain zero-concentration F- in toothpaste but difficult. Calibration curve is possible with b) and d).

[7] E = const – 0.0592 log [Cl^-]
-0.455 V = const – 0.0592 log [4.33e-3]
Const = -0.595

-0.474 = -0.595 – 0.0592 log [Cl^-]
[Cl^-] = 9.04e-3 M

[8] E = const – 0.0592 log[F^-]

Let x = conc of F- in sample

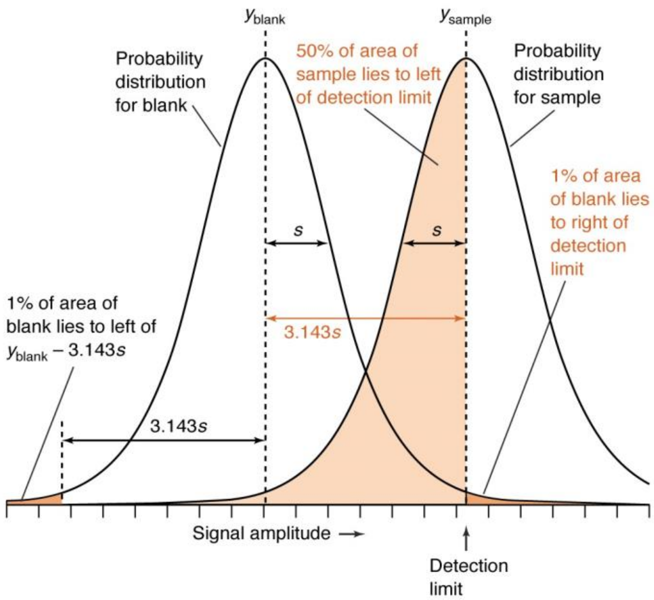
Conc of F- after dilution = (5.00/10.00)*1.66e-3 = 8.30e-4 M

First response: -0.255 = const – 0.0592 log (x)
Second: -0.301 = const – 0.0592 log (x + 8.30e-4)

Subtract the 2 equations:

-0.255 = const – 0.0592 log (x)
-(-0.301 = const – 0.0592 log (x + 8.30e-4))

0.0460 = 0.0592 log (x + 8.30e-4)/x
x = 6.97e-5 M sample = 2x = 3.33e-4 M



The LOD is where we are 99% confident that the signal we are measuring for a low concentration analyte (sample in the figure) is not the blank. This requires the mean signal values for the blank and the low concentration measurement is 3.1 standard deviations apart.

LOD = 3s/m