LABORATORY REPORT COVER PAGE

GROUP NUMBER T1

EXPERIMENT NUMBER 4

TITLE: Equilibrium Electrochemistry: Cell Potential and Activity

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OVERALL GRADE 100/100

ROLE ASSIGNMENTS

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SUMMARY OF CONCLUSIONS

An electrochemical cell was constructed using amalgaMAted Pb / Pb and Ag – AgCl electrodes, in Pb(NO3)2 and KCl solutions, respectively. Cell potentials were measured under varying conditions, including sparging, stirring, amalgated versus pure lead electrode, and the use of a new Ag – AgCl wire versus commercially made Ag – AgCl reference cell. All cell potentials were found to be consistently lower than expected cell potential values. In addition, the aforementioned parameters had significant effect on the cell potential measured with the exception of pure Pb electrode. Cell potential with the pure Pb electrode was found to be significantly different from that of the control (amalgated Pb). However, the cell potential with pure Pb was still 3.99% different from the expected cell potential. Proposed temperature difference was also inadequate to explain the observed phenomenon.

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Results

In this experiment, the standard electrochemical cell is set up as: sparging, stirring, unsandpapered, lead with Hg.

Figure 1

with Commercial Ag – AgCl Cell					New Ag – AgCl Electrode				
type	m	ideal E (mV)	experimental E (mv)	% deviation from ideal	type	m	ideal E (mV)	experimental E (mv)	% deviation from ideal
Original									
	0.0001	461.1877	433	-6.11198		0.0001	461.2	428	-7.19614
	0.001	432.6771	414	-4.31663		0.001	432.7	410	-5.2411
	0.01	406.233	393	-3.25749		0.01	406.2	389	-4.24214
Lead w/out Hg			E(mV)		Lead w/out Hg			E(mV)	
	0.0001	461.1877	438	-5.02782		0.0001	461.2	434	-5.89515
	0.001	432.6771	420	-2.92991		0.001	432.7	415	-4.08551
	0.01	406.233	396	-2.519		0.01	406.2	392	-3.50365
No Stirring			E(mV)		No Stirring			E(mV)	
	0.0001	461.1877	434	-5.89515		0.0001	461.2	431	-6.54564
	0.001	432.6771	415	-4.08551		0.001	432.7	412	-4.77887
	0.01	406.233	390	-3.99598		0.01	406.2	385	-5.2268
No Sparging			E(mV)		No Sparging			E(mV)	
	0.0001	461.1877	430	-6.76247		0.0001	461.2	424	-8.06346
	0.001	432.6771	417	-3.62327		0.001	432.7	413	-4.54775
	0.01	406.233	390	-3.99598		0.01	406.2	385	-5.2268
sandpapered electrode			E(mV)		sandpapered electrode			E(mV)	
	0.0001	461.1877	429	-6.9793		0.0001	461.2	425	-7.84663
	0.001	432.6771	416	-3.85439		0.001	432.7	413	-4.54775
	0.01	406.233	391	-3.74982		0.01	406.2	386	-4.98064
REPEAT lead w/out Hg (sparging, stirring)									
	0.0001	461.1877	427	-7.41297		0.0001	461.2	405	-12.1833
	0.001	432.6771	413	-4.54775		0.001	432.7	404	-6.62782
	0.01	406.233	387	-4.73447		0.01	406.2	292	-28.1201

REPEAT lead w/out Hg, newly made 0.001 solution (from powder)	0.001	432.6771	411	-5.00998	0.001	432.7	406	-6.16558

Other Observations:
Sandpapered electrode value starts off the highest, but gets off lower rapidly with time. E (mV) value drops with time, sometimes staying at a consistent value, sometimes dropping lower. Example: repeat of the original at 0.1mM starts at 477 mV and drops until 418.

Figure 2

	Original	**no Hg**	**no Stir**	**no Sparg**	**Sanded**
Commercial Ag – AgCl cell	433	438	434	430	429
	414	420	415	417	416
	393	396	390	390	391
New Ag – AgCl wire	428	434	431	424	425
	410	415	412	413	413
	389	392	385	385	386
t_{stat}	---	-8.3666	0	0.964486	0.976375
t_{crit}	---	2.570578	2.570578	2.570578	2.570578
diff?	---	TRUE	FALSE	FALSE	FALSE

In the table above, the control system is compared to the other experimental systems. The control system included sparging, stirring, and un-sandpapered amalgamated Pb electrode. T-tests for two averages were performed by comparing the averages of all the potentials read for a particular system for all concentrations.

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Analysis

In Figure 2 above, it can be seen that with the exception of the Pb versus amalgated Pb electrode, tested parameters yield no significant differences in the results. For example, sparging versus no-sparging had no overall significance of the potential of the cell. As expected, the concentrations of the cells decreased the voltage increased; this is probably due to the ions ability to flow through the aqueous solutions. NO-AT EQUILIBRIUM NOTHING FLOWS The higher concentrations were analogous to having a higher resistance in the circuit, HIGH CONC MEANS LOW RESISTANCEand thus it was more difficult for the ions to flow though the higher concentration solutions. Sand-papering and stirring, are examples of parameters that also had no effect on the overall cell potential.

Of the variables that we measured in this experiment, only the use of amalgamated Pb (Pb + Hg) versus the pure lead electrode has a significant difference (t stat of –8.3666 compared to t critical value of 2.570578). The use of pure lead electrode apparently produces higher cell potential, which is favourable since experimental control potential is 5.06% lower than the average expected (ideal) cell potential. However, the average pure lead electrode is still 3.99 % lower than the ideal (expected) cell potential.

The results suggest that none of the variables (Ag wire versus probe, lead electrode versus amalgamated electrode, sparging, stirring, sandpapering) were a significant factor deterring the cell potential from expected values. Other force(s) must be at work.GOOD POINT

Cell potential is affected by the Nernst equation $\varepsilon = \varepsilon_0 - (RT/nF)\ln Q$, in which Q is defined by activities of the metal / ions involved. Since all the other tested variables had no effect, we proposed that the temperature was the factor affecting the total potential of the cell.

Initially, it was suspected that, since during the experiment, it was observed that the stirring plate felt warm, the rise in the temperature of the electrolytes could lead to inaccuracy in the measurement of the cell potential.

However, according to the Nernst equation, if T increases, total cell potential should increase instead of decrease. This is because the natural log term is always negative at low concentration. Decrease in temperature, not increase in temperature, is more likely in explaining the observed phenomenon. It was therefore proposed that perhaps the room temperature, recorded to be 22 degrees Celsius, caused deviation in the cell potential measurement. This, however, was also not the dominant factor affecting the measurement. For example at 25 ^{0}C the cell potential of the 0.1mM solution is 432.7mV, but as the temperature is decreased by 3^0 C the cell potential changes only by 1mV, a difference that does not adequately describe the deviation that is observed experimentally. Thus our hypothesis is proven incorrect. NOW THAT IS WHAT I CALL REAL ANALYSIS! THAT IS THE CRUX OF SCIENTIFIC ANALYSIS-BRAVO!

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References

Castellan “Physical Chemistry” Chapter 17
Litt, Mitchell “BE 309 Bioengineering Laboratory III Laboratory Manual”, Experiment 4