

Homework Set #1

7 points total

1. Measures of Concentration & Charge Balance

4 points for #1

In 2008 Northampton MA completed construction of a filtration plant to treat their surface water supplies (see: <http://www.ecs.umass.edu/eve/background/Utilities/DWT/MA/Northampton/>). This facility is located near one of Northampton's two major surface water sources, the Mountain Street Reservoir in Williamsburg. This source is characterized as low-alkalinity and low-hardness, quite typical of most surface waters in New England. On March 19, 1997, a sample of the Mountain Street Reservoir water was collected and submitted for chemical analysis. The results are shown below.

Constituent	Concentration	Units
Turbidity	0.59	NTU
TDS	29	mg/L
Color	10	Color units
Odor	1	TON
pH	6.75	Log units
Total Alkalinity	13	mg-CaCO ₃ /L
Total Hardness	20	mg-CaCO ₃ /L
Calcium	6.7	mg/L
Magnesium	0.89	mg/L
Aluminum	<0.05	mg/L
Potassium	<1	mg/L
Sodium	5.0	mg/L
Iron	<0.05	mg/L
Manganese	0.016	mg/L
Sulfate	5.9	mg/L
Chloride	3.0	mg/L
Silver	<0.005	mg/L
Copper	<0.01	mg/L
Zinc	<0.05	mg/L
TOC ¹	3	mg/L

¹ Not measured; estimated from historical data

a. Estimate the bicarbonate concentration assuming that all of the measured alkalinity is bicarbonate.

0.5 points

$$\begin{aligned}
 [HCO_3^-] &\equiv Alk \\
 &= 13 \frac{mg - Alk}{L} \left(\frac{1meq - Alk}{50mg - Alk} \right) \left(\frac{1mM - HCO_3^-}{1meq - Alk} \right) \left(\frac{61.019mg - HCO_3^-}{1mM - HCO_3^-} \right) \\
 &= 15.86 \frac{mg - HCO_3^-}{L} \\
 &\approx 16 \frac{mg - HCO_3^-}{L} \\
 &\approx 0.26mM
 \end{aligned}$$

b. Calculate the ionic strength

1.0 points

$$I = \frac{1}{2} \sum m_i z_i^2$$

Now its important to recognize that several of the constituents in the table above are presented as being below a certain value (probably the lab's method detection limit). It may be safest to assume a value of zero for all of these. This would give a lower bound to the estimates of ionic strength and ion charge. When calculating this, be careful to include the bicarbonate.

	Constituent	Conc.	Units	GFW	mM/L	z	meq/L	0.5* mz ²
Cations	Calcium	6.7	mg/L	40.08	0.167166	2	0.334331	0.334331
	Magnesium	0.89	mg/L	24.305	0.036618	2	0.073236	0.073236
	Sodium	5	mg/L	22.989	0.217495	1	0.217495	0.108748
	Manganese	0.016	mg/L	54.938	0.000291	2	0.000582	0.000582
Anions	Sulfate	5.9	mg/L	96.0636	0.061418	2	0.122835	0.122835
	Chloride	3	mg/L	35.453	0.084619	1	0.084619	0.04231
	Bicarbonate	15.86	mg/L	61	0.26	1	0.26	0.13
	Sum					I =	0.812042	

Therefore, in the traditional equivalent-based units:

$$I = 8.12 \times 10^{-4} \text{ (molar units)}$$

c. Determine the “analytical” concentration of $[H^+]$ using the Debye-Huckel equation.

0.5 points

$$\begin{aligned} \log \gamma &= -0.5z^2 \sqrt{I} \\ \log \gamma_{H^+} &= -0.5 \sqrt{0.812 \times 10^{-3}} \\ &= -0.01425 \\ \gamma_{H^+} &= 0.9677 \end{aligned}$$

$$\begin{aligned} [H^+] &= \frac{\{H^+\}}{\gamma_{H^+}} \\ &= \frac{10^{-6.75}}{0.9677} \\ &= 10^{-6.736} = 1.838 \times 10^{-7} \end{aligned}$$

d. Perform a charge balance on this water based on the measured concentrations. Is there apparent excess charge, and if so, why?

1.0 points

	Constituent	Conc.	Units	GFW	mM/L	Z	sum(c*z)
Cations	Calcium	6.7	mg/L	40.08	0.167166	2	0.625645
	Magnesium	0.89	mg/L	24.305	0.036618	2	
	Sodium	5	mg/L	22.989	0.217495	1	
	Manganese	0.016	mg/L	54.938	0.000291	2	
Anions	Sulfate	5.9	mg/L	96.0636	0.061418	2	0.467454
	Chloride	3	mg/L	35.453	0.084619	1	
	Bicarbonate	15.86	mg/L	61	0.26	1	
	Sum						mM

Total Cations = 0.626 meq/L

Total Anions = 0.467 meq/L

Note that the anions and cations are added together separately. This allows one to assess the relative degree of imbalance. In this case, there's a substantial imbalance; about 25% of the total charge appears to be missing (negative charges). Why so large? Analytical error? A major constituent overlooked?

I would say that the natural organic matter (NOM), as represented by the TOC of 3 mg/L is a likely candidate. This material (NOM) is always negatively charged, and a typical "charge density" is 20 meq/g-C. If we use this along with the TOC, we get an additional 0.06 meq/L negative charge from the NOM. This would bring the negative charges up to about 0.53 meq/L. Much better, but this still suggests we may be missing something. Some of this could come from nitrate which wasn't measured. One can't ignore the possibility of analytical error as well.

e. Calculate the "theoretical" TDS based on the chemical analysis above and compare with the actual measured TDS. Are they different, and if so why do you think this is the case?

1.0 points

Calculation of TDS is normally a simple matter of adding the concentrations of known constituents (ignoring any water). Bicarbonate may be partly lost depending on the cations present and the temperature used in the TDS determination. The organic matter (NOM) may also be partly lost when using higher temperatures. The total mass of NOM can be estimated by assuming that it is usually 50% carbon by weight. This gives 4 possible answers ranging from 21.5 to 43.4 mg/L. If we assume that half of the bicarbonate and TOC are lost, this would give us a TDS of about 31 mg/L, a number that is not too far from the analytical determination (29 mg/L).

#	TDS (mg/L)	Calculation	Explanation
1	21.5	Sum of all ions above except bicarbonate	Low bound; ignoring all Carbon compounds; assuming they volatilize t
2	27.5	Same as #1, but with 2*TOC	Assumes that bicarbonate volatilizes but NOM remains
3	37.4	Same as #1, but with bicarbonate	Assuming bicarbonate remains, but NOM is volatilized
4	43.4	Same as #3, but with 2*TOC	Assumes all C-compounds remain

2. Activity

A series of 10^{-3} F HCl solutions are prepared², each solution containing a different concentration of KCl in the range of 0.01 F to 0.50 F. Plot pH (i.e., $-\log\{H\}$) vs log I using:

- Davies Equation;
- Extended Debye-Huckel Equation.

2.0 points

Solution to 2

Ionic Strength is calculated by considering both the HCl and the KCl added:

$$I = \frac{1}{2} \sum m_i z_i^2$$

Extended Debye-Hückel equation:

$$\log f = -0.5z^2 \frac{\sqrt{I}}{1 + 0.33a\sqrt{I}}$$

² F refers to Formality, which is the concentration in moles per liter that would exist if the material added to the solvent did not dissociate or react in any way to change its chemical structure

Davies Equation

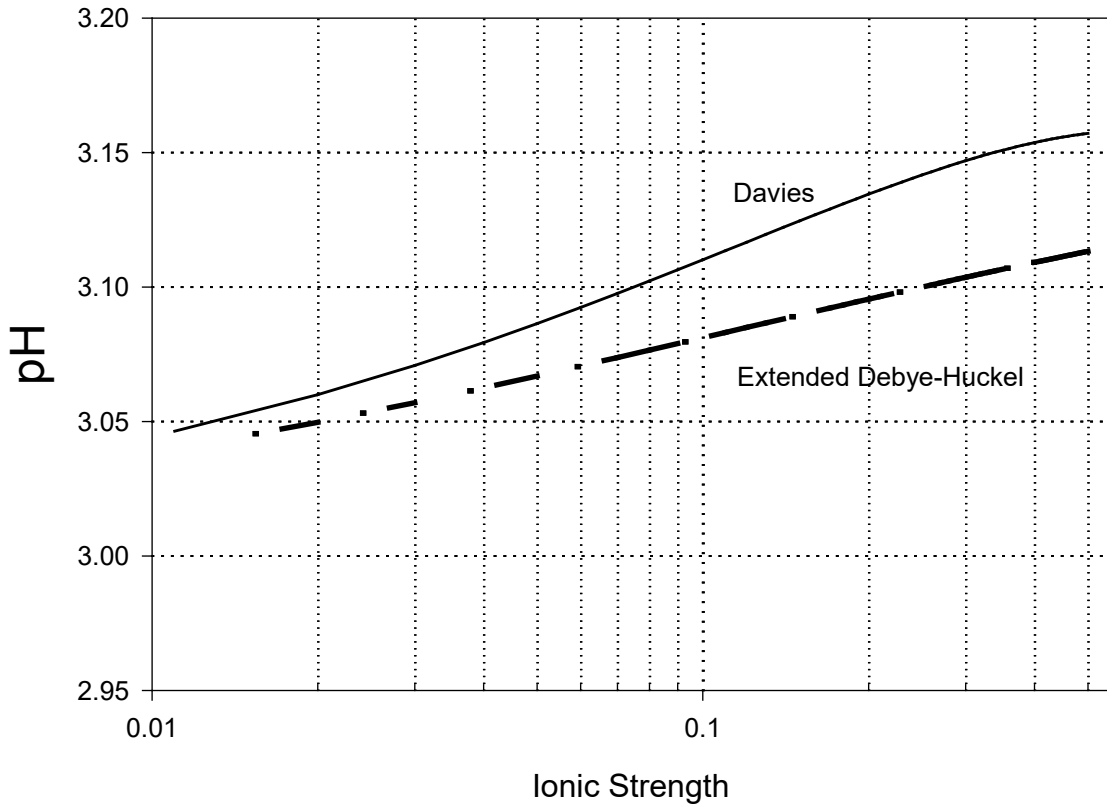
$$\log f = -0.5z^2 \left(\frac{\sqrt{I}}{1 + \sqrt{I}} - 0.2I \right)$$

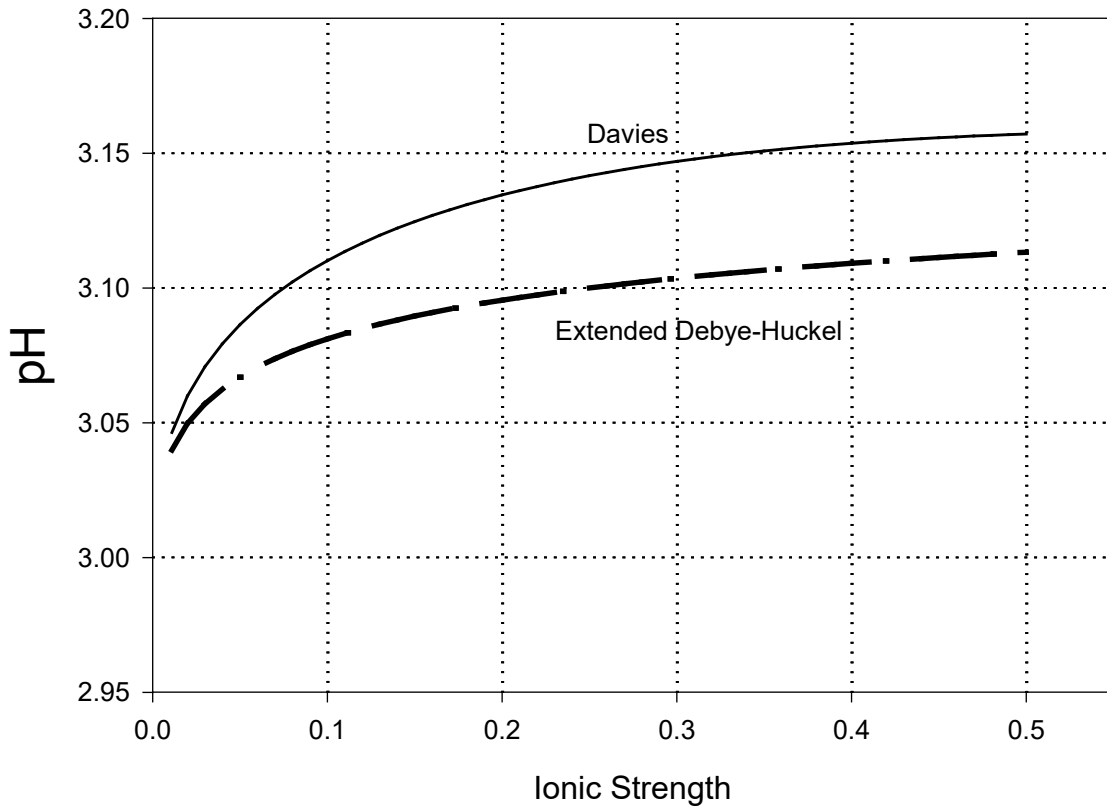
And for this case where 1 mM of a strong acid is added:

$$pH = -\log\{H^+\} = -\log f - \log[H^+] = -\log f + 3$$

[KCl]	I	Davies			Extended D-H		
		log f	f	{H}	log f	f	{H}
0.01	0.011	-0.04636	0.898747	3.046363	-0.03989	0.912243	3.03989
0.02	0.021	-0.06119	0.868589	3.061186	-0.0505	0.890222	3.050502
0.03	0.031	-0.07175	0.847706	3.071755	-0.05761	0.875777	3.057606
0.04	0.041	-0.08009	0.831583	3.080094	-0.06298	0.865002	3.062983
0.05	0.051	-0.08701	0.818439	3.087014	-0.06731	0.856422	3.067312
0.06	0.061	-0.09293	0.807362	3.092932	-0.07093	0.849311	3.070933
0.07	0.071	-0.0981	0.797814	3.098098	-0.07404	0.843253	3.074042
0.08	0.081	-0.10268	0.78945	3.102675	-0.07676	0.837988	3.076762
0.09	0.091	-0.10678	0.782032	3.106776	-0.07918	0.833342	3.079177
0.1	0.101	-0.11048	0.775388	3.110481	-0.08135	0.82919	3.081346
0.11	0.111	-0.11385	0.769391	3.113853	-0.08331	0.825444	3.083312
0.12	0.121	-0.11694	0.763943	3.116939	-0.08511	0.822036	3.085109
0.13	0.131	-0.11978	0.758968	3.119776	-0.08676	0.818914	3.086762
0.14	0.141	-0.1224	0.754404	3.122396	-0.08829	0.816036	3.088291
0.15	0.151	-0.12482	0.750202	3.124822	-0.08971	0.813371	3.089711
0.16	0.161	-0.12708	0.746319	3.127075	-0.09104	0.81089	3.091038
0.17	0.171	-0.12917	0.742722	3.129173	-0.09228	0.808573	3.092281
0.18	0.181	-0.13113	0.739382	3.131131	-0.09345	0.806401	3.093449
0.19	0.191	-0.13296	0.736272	3.132961	-0.09455	0.804357	3.094551
0.2	0.201	-0.13467	0.733373	3.134675	-0.09559	0.802429	3.095593
0.21	0.211	-0.13628	0.730666	3.136281	-0.09658	0.800606	3.096581
0.22	0.221	-0.13779	0.728134	3.137789	-0.09752	0.798878	3.09752
0.23	0.231	-0.1392	0.725764	3.139205	-0.09841	0.797236	3.098413
0.24	0.241	-0.14054	0.723542	3.140536	-0.09927	0.795673	3.099265
0.25	0.251	-0.14179	0.721459	3.141789	-0.10008	0.794182	3.10008
0.26	0.261	-0.14297	0.719503	3.142967	-0.10086	0.792758	3.100859
0.27	0.271	-0.14408	0.717666	3.144077	-0.10161	0.791395	3.101606
0.28	0.281	-0.14512	0.715941	3.145123	-0.10232	0.79009	3.102324
0.29	0.291	-0.14611	0.71432	3.146107	-0.10301	0.788837	3.103013
0.3	0.301	-0.14703	0.712796	3.147035	-0.10368	0.787633	3.103676
0.31	0.311	-0.14791	0.711363	3.147909	-0.10432	0.786475	3.104315
0.32	0.321	-0.14873	0.710017	3.148731	-0.10493	0.785359	3.104932
0.33	0.331	-0.14951	0.708753	3.149505	-0.10553	0.784284	3.105527
0.34	0.341	-0.15023	0.707565	3.150234	-0.1061	0.783247	3.106101
0.35	0.351	-0.15092	0.706449	3.150919	-0.10666	0.782244	3.106658
0.36	0.361	-0.15156	0.705403	3.151563	-0.1072	0.781275	3.107196
0.37	0.371	-0.15217	0.704422	3.152167	-0.10772	0.780338	3.107717

0.38	0.381	-0.15273	0.703504	3.152734	-0.10822	0.77943	3.108223
0.39	0.391	-0.15326	0.702644	3.153264	-0.10871	0.778549	3.108714
0.4	0.401	-0.15376	0.701841	3.153761	-0.10919	0.777696	3.10919
0.41	0.411	-0.15422	0.701092	3.154225	-0.10965	0.776867	3.109653
0.42	0.421	-0.15466	0.700394	3.154657	-0.1101	0.776063	3.110103
0.43	0.431	-0.15506	0.699746	3.15506	-0.11054	0.775281	3.110541
0.44	0.441	-0.15543	0.699144	3.155433	-0.11097	0.774521	3.110967
0.45	0.451	-0.15578	0.698588	3.155779	-0.11138	0.773781	3.111382
0.46	0.461	-0.1561	0.698074	3.156098	-0.11179	0.773061	3.111786
0.47	0.471	-0.15639	0.697603	3.156392	-0.11218	0.772359	3.112181
0.48	0.481	-0.15666	0.697171	3.156661	-0.11257	0.771676	3.112565
0.49	0.491	-0.15691	0.696778	3.156906	-0.11294	0.771009	3.11294
0.5	0.501	-0.15713	0.696421	3.157128	-0.11331	0.770359	3.113307





3. Stable Isotope Ratios

Blasch and Bryson (2007; Groundwater 45:3:294) investigated stable isotopes in groundwaters across central Arizona. Their average isotopic ratio for the four major zones are listed below.

1.0 points

Subbasin	$\delta^2\text{H}$ (‰)	$\delta^{18}\text{O}$ (‰)
Little Chino	-70	-9.7
Big Chino	-75	-10.3
Verde Valley North	-84	-11.6
Verde Valley South	-78	-10.6

- a. If the Verde River under base flow conditions is fed only by the Big Chino, Verde Valley North and Verde Valley South aquifers, and the average deltas for the Verde River water are: $\delta^2\text{H} = -81.3$ and $\delta^{18}\text{O} = -11.17$, estimate the percent composition of the Verde River base flow from each of the three aquifers.

0.5 points

These can be calculated from a weighted mix of the deltas and knowing that Little Chino does not contribute and the total of the other three must equal 100%. This gives you;

$$\begin{aligned}\delta^{2H} &= -81.3 = -75f_{BC} - 84f_{VVN} - 78f_{VVS} \\ \delta^{18O} &= -11.17 = -10.3f_{BC} - 11.6f_{VVN} - 10.6f_{VVS} \\ 1 &= f_{BC} + f_{VVN} + f_{VVS}\end{aligned}$$

Solving three equations and three unknowns:

Subbasin	Percent composition
Little Chino	0%
Big Chino (BC)	10%
Verde Valley North (VVN)	60%
Verde Valley South (*VVS)	30%

- b. Calculate the deltas (δ^{2H} and δ^{18O}) for water vapor in equilibrium with the Verde River water at 30C.

0.5 points

Calculate R-water for each isotope from:

$$\delta = \left(\frac{R_{sample} - R_{standard}}{R_{standard}} \right) \times 1000$$

For the hydrogen delta

$$\delta^{2H} = -81.3 = \left(\frac{R_{liquid} - 0.00015576}{0.00015576} \right) \times 1000$$
$$R_{liquid} = 0.0001431$$

Then using the Dansgaard figure to get an equilibrium R_{vapor} :

$$R_{vapor} = \frac{1}{\alpha} R_{liquid}$$

For 30C, based on lecture 4, slide 7:

$$\alpha_D \equiv \frac{R_{liquid}}{R_{vapor}} \equiv \frac{\left(\frac{^2H}{^1H} \right)_{liquid}}{\left(\frac{^2H}{^1H} \right)_{vapor}} = 1.07$$

And incorporating the alpha from the Dansgaard slide:

$$R_{vapor} = \frac{1}{1.07} (0.0001431) = 0.000134$$

And now calculating the delta for this vapor

$$\delta^{2H} = \left(\frac{0.000134 - 0.00015576}{0.00015576} \right) \times 1000 = -141.4$$

For the oxygen delta

$$\delta^{18}\text{O} = -11.7 = \left(\frac{R_{\text{liquid}} - 0.0020052}{0.0020052} \right) \times 1000$$

$$R_{\text{liquid}} = 0.001983$$

Then using the Dansgaard figure to get an equilibrium R_{vapor} :

$$R_{\text{vapor}} = \frac{1}{\alpha} R_{\text{liquid}}$$

For 30C, based on lecture 4, slide 7:

$$\alpha_{18} \equiv \frac{R_{\text{liquid}}}{R_{\text{vapor}}} \equiv \frac{\left(\frac{^{18}\text{O}}{^{16}\text{O}} \right)_{\text{liquid}}}{\left(\frac{^{18}\text{O}}{^{16}\text{O}} \right)_{\text{vapor}}} = 1.0082$$

And incorporating the alpha from the Dansgaard slide:

$$R_{\text{vapor}} = \frac{1}{1.0082} (0.001983) = 0.001967$$

And now calculating the delta for this vapor

$$\delta^{18}\text{O} = \left(\frac{0.001967 - 0.0020052}{0.0020052} \right) \times 1000 = -19.2$$

In summary:

Isotope	α (from L4, S7)	R-vapor	R-vapor	Deltas
^2H	1.07	0.000143	0.000134	-141.4
^{18}O	1.0082	0.001983	0.001967	-19.2