

Analytical Chemistry Lecture 4 Workshop Solutions
Oct. 06, 2004

1. What is the ionic strength of a solution that is 0.050 M in KNO₃ and 0.10 M in Na₂SO₄?

In order to calculate ionic strength we need to know the concentration of each ion species in solution. First some solution chemistry. What do we know about the solubility of nitrate compounds? Every nitrate salt is soluble. What about the solubility of sodium salts? Again all soluble. What about sulfates? Most are soluble except Ca, Sr, Ba, Ra, Ag, Hg₂²⁺, and Pb. How do I know this? I look in Appendix F which gives the solubility products of substances that are only sparingly soluble.

Now, when we write a solution of KNO₃, we assume that the salt is completely dissociated as ions. So [K⁺] = 0.050 M; [NO₃⁻] = 0.050 M; [Na⁺] = 0.20 M; [SO₄²⁻] = 0.10 M

$$\mu = \frac{1}{2}[(0.050 \times 1^2) + (0.050 \times 1^2) + (0.20 \times 1^2) + (0.10 \times 2^2)] = 0.35 \text{ M}$$

2. Determine the activity coefficient for Hg²⁺ (the mercuric ion) in a solution that has an ionic strength of 0.085 first using the Debye-Huckel equation and then using Table 8-1. Compare the two answers.

To use the equation we need, ionic strength (0.085), ionic charge +2, and the effective ionic radius, given in table 8-1. $\alpha = 500 \text{ pm}$

$$\log \gamma_{\text{Hg}^{2+}} = \frac{-0.51 (2^2) \sqrt{0.085}}{1 + (500/305 * \sqrt{0.085})} = -\frac{0.59475}{1.47795} = -0.402; \quad \gamma_{\text{Hg}^{2+}} = 10^{-0.402} = 0.396$$

Now we get the activity coefficient from Table 8-1. First we note that the solution activity falls between 0.05 M and 0.10 M

From the table values are at $\mu =$	0.05	0.085	0.10	values of x
	0.465	?	0.380	values of y

Interpolation involves assuming there the property involved forms a straight line between given data points and that we can use this assumption to estimate a value of y for a known value of x.

Harris does this using the following equation

$$\frac{\text{unknown y interval}}{\Delta y \text{ given}} = \frac{\text{known x interval}}{\Delta x \text{ given}}$$

$$\frac{0.465 - y}{0.465 - 0.380} = \frac{0.05 - 0.085}{0.05 - 0.10} = \frac{-0.035}{-0.05} = 0.70$$

$$\frac{0.465 - y}{0.085} = 0.70 \rightarrow 0.465 - y = 0.70 * 0.085 = 0.0595$$

$$y = 0.465 - 0.0595 = 0.406$$

The values are fairly close to each other. We are getting close to 0.10 M where the equation starts to break down.

3. (Problem 8-13) Use activities to find the barium ion concentration in a 0.100 M $(\text{CH}_3)_4\text{NIO}_3$ solution saturated with $\text{Ba}(\text{IO}_3)_2$.

In order to use activities we need to determine the ionic strength of the solution. What are the ions in the substance $(\text{CH}_3)_4\text{NIO}_3$? If you don't know you can use Table 8-1 to find them. $(\text{CH}_3)_4\text{N}^+$ tetramethylammonium ion, IO_3^- iodate ion. All ammonium ion compounds are soluble.

So the $[(\text{CH}_3)_4\text{N}^+] = 0.100 \text{ M}$ and $[\text{IO}_3^-] = 0.100 \text{ M}$

$$\mu = \frac{1}{2} [(0.100 \times 1^2) + (0.100 \times 1^2)] = 0.100 \text{ M}$$

Barium iodate is only partly soluble and has $K_{sp} = 1.5 \times 10^{-9}$.

The dissociation reaction is



table

before	solid	0	0.100
after	solid	x	0.100 + 2x

using activities $K_{sp} = a_{\text{Ba}} \cdot a_{\text{IO}_3}^2 = \gamma_{\text{Ba}} [\text{Ba}^{2+}] \cdot \gamma_{\text{IO}_3}^2 [\text{IO}_3^-]^2$

from Table 8-1, at $\mu = 0.100 \text{ M}$, $\gamma_{\text{Ba}} = 0.38$ and $\gamma_{\text{IO}_3} = 0.775$

after the reaction comes to equilibrium, the equation becomes

$$1.5 \times 10^{-9} = 0.38 [x] \cdot (0.775)^2 (0.100 + 2x)^2 \quad \text{Let's assume that } 2x \text{ is small compared to } 0.100$$

$$1.5 \times 10^{-9} = 0.38 [x] \cdot (0.775)^2 (0.100)^2$$

$$\frac{1.5 \times 10^{-9}}{2.28 \times 10^{-3}} = x = [\text{Ba}^{2+}] = 6.6 \times 10^{-7} \text{ M}$$

4. Describe the set up of the following problem. (Problem 8-15a) Using K_{sp} for calcium sulfate ($K_{sp} = 2.4 \times 10^{-5}$), determine the activity coefficients for both ions and calculate the $[\text{Ca}^{2+}]$ in a saturated aqueous solution of CaSO_4 .

We don't know the ionic strength of the solution. So we first solve the problem assuming that the activity coefficients are 1.

	$\text{CaSO}_4(\text{s})$	\rightleftharpoons	Ca^{2+}	$+$	SO_4^{2-}
Initial	solid		0		0
Final	solid		x		x

$$K_{sp} = 2.4 \times 10^{-5} = [\text{Ca}^{2+}] [\text{SO}_4^{2-}] = x^2 \rightarrow x = \sqrt{(2.4 \times 10^{-5})} = 4.90 \times 10^{-3} \text{ M}$$

Now we calculate the ionic strength and then activity coefficients for the two ions

$$\mu = \frac{1}{2} [(0.00490 \times 2^2) + (0.00490 \times 2^2)] = 0.0196 \text{ M}$$

now we interpolate in table 8-1 for the two activity coefficients or use the Debye-Huckel equation. Let's interpolate

	0.01	0.0196	0.05
for Ca^{2+}	0.675	y	0.485
for SO_4^{2-}	0.660	y	0.445

$$\text{for Ca} \quad \frac{0.675 - y}{0.675 - 0.485} = \frac{0.01 - 0.0196}{0.01 - 0.05} = \frac{-0.0096}{-0.04} = 0.24$$

$$\frac{0.675 - y}{0.19} = 0.24 \rightarrow 0.675 - y = 0.19 * 0.24 = 0.0456$$

$$y = 0.675 - 0.0456 = 0.629_4$$

$$\text{for SO}_4 \quad \frac{0.660 - y}{0.660 - 0.445} = \frac{0.01 - 0.0196}{0.01 - 0.05} = \frac{-0.0096}{-0.04} = 0.24$$

$$\frac{0.660 - y}{0.215} = 0.24 \rightarrow 0.660 - y = 0.215 * 0.24 = 0.0516$$

$$y = 0.660 - 0.0516 = 0.608_4$$

Round 2: now use activity coefficients

$$K_{sp} = 2.4 \times 10^{-5} = \gamma_{\text{Ca}} [\text{Ca}^{2+}] \gamma_{\text{SO}_4} [\text{SO}_4^{2-}] = 0.629 (x) 0.608 (x)$$

$x = \sqrt{(2.4 \times 10^{-5}) / (0.629 \cdot 0.608)} = 7.92 \times 10^{-3} \text{ M}$ and increase of more than a factor of 2 from the first round.

Now calculate a new ionic strength and new activity coefficients and do it again. Keep repeating until the answer x stops changing to 2 sig figs. This happens on the 5th round.

The final answer is $9.2 \times 10^{-3} \text{ M}$. Harris got $9.9 \times 10^{-3} \text{ M}$ using the Debye-Huckel equation for each round of iteration.

8-15b) The observed total concentration of dissolved calcium is 15-19 mM. Explain.

For some reason more calcium sulfate goes into solution than the calculate allows. Other ions in solution would change the ionic strength, but the only other ions are H^+ and OH^- which are at concentrations near 10^{-7} M . So the answer is not the effect of other ions.

The explanation lies in the fact that cations and anions with multiple charges often form soluble undissociated species in solution. This phenomenon is discussed in Box 8-1 on page 152.

Calcium sulfate must form a neutral and soluble $\text{CaSO}_4(\text{aq})$ species that accounts for the additional dissolved calcium sulfate at equilibrium. These species are rarely considered by laboratory chemist, but can play an enormous role in geological systems.

Environmental Analysis 2004
Analytical Chemistry Problem Set 2

1-25. It is recommended that drinking water contain 1.6 ppm fluoride (F⁻) for prevention of tooth decay. Consider a reservoir with a diameter of 4.50×10^2 m and a depth of 10.0 m. (The volume is $\pi r^2 h$, where r is the radius and h is the height.) How many grams of F⁻ should be added to give 1.6 ppm? How many grams of sodium fluoride, NaF, contain this much fluoride?

We know the concentration of fluoride in ppm and presumably we can calculate the volume of the reservoir. The problem asks for grams of fluoride. So we need to convert the concentration to moles per liter, multiply by the volume to get total moles and convert moles to grams of fluoride.

a)

1.6 ppm is 1.6×10^{-6} g/g of solution or 1.6 mg / kg of solution. For water, 1 L has a mass of 1 kg. There are 1000 L in a cubic meter (*Handbook of Chemistry and Physics.*) So

$$1.6 \text{ mg F/kg} \times 1 \text{ kg/1 L} \times 1000 \text{ L/m}^3 \times \pi \times (4.50 \times 10^2 \text{ m}/2)^2 \times 10.0 \text{ m} \times 1 \text{ g F/ 1000 mg F} =$$

$$2.54 \times 10^6 \text{ g F}$$

b) We now convert mass of F to mass of NaF. Since there is one mole of F in each mole of NaF, we can use a ratio of the masses directly. AM of F is 18.998 and AM of Na is 22.9898.

$$2.54 \times 10^6 \text{ g F} \times 41.988 \text{ g NaF}/18.998 \text{ g F} = 5.6 \times 10^6 \text{ g NaF}$$

- 3-5.** a) $1.021 + 2.69 = 3.71$ 3 sig figs
 b) $12.3 - 1.63 = 10.7$ 3 sig figs
 c) $4.32 \times 9.2 = 4.0 \times 10^1$ 2 sig figs, writing 40 does not convey 2 sig figs
 d) $0.0602/2.113 \times 10^4 = 2.85 \times 10^{-6}$ 3 sig figs
 e) $\log(4.218 \times 10^{12}) = 12.6251$ 4 sig figs
 f) $\text{antilog}(-3.22) = 6.0 \times 10^{-4}$ 2 sig figs
 g) $10^{2.384} = 242$ 3 sig figs

- 3-12.** Answer (a) Carmen. - accurate and precise
 (b) Cynthia - accurate but not precise
 (c) Chastity - precise but not accurate
 (d) Cheryl - neither precise nor accurate

3-15a,b,g Find the absolute and percent relative uncertainty and express each answer with a reasonable number of significant figures.

a) $9.23 (\pm 0.03) + 4.21 (\pm 0.02) - 3.26 (\pm 0.06) = 10.18$ (has 4 sig figs due to addition)

for addition and subtraction we use absolute uncertainties to calculate the uncertainty in the answer. $e = \sqrt{(0.03)^2 + (0.02)^2 + (0.06)^2} = 0.07$

as percent uncertainty $0.07/10.18 \times 100\% = 0.689\% = 0.7\%$

the answer is $10.18 (\pm 0.07) (\pm 0.7\%)$

b) $91.3 (\pm 1.0) \times 40.3 (\pm 0.2) / 21.1 (\pm 0.2) = 174$ (has 3 sig figs due to mult/divide)

for multiplication and division we use percent uncertainties to calculate uncertainty in answer.

$$1.0/91.3 \times 100\% = 1.10\%; \quad .2/40.3 \times 100\% = 0.50\%; \quad .2/21.1 \times 100\% = 0.95\%$$

so we now have

$$91.3 (\pm 1.10\%) \times 40.3 (\pm 0.50\%) / 21.1 (\pm 0.95\%) = 174$$

$$\% \text{ uncertainty} = \sqrt{(1.10)^2 + (0.50)^2 + (0.95)^2} = 1.54\%$$

$$\text{converting back to absolute uncertainty } 1.54\%/100\% \times 174 = 2.68 = 3$$

answer $174 (\pm 3) (\pm 1.5\%)$

$$\text{g) } \log [3.14 (\pm 0.05)] = 0.497$$

$$\text{For } y = \log x, \quad e_y = 0.43429 e_x/x = 0.43429 (0.05/3.14) = 0.006915$$

$$\text{In } \% \text{ uncertainty this is } .006915/.4969 \times 100\% = 1.39\%$$

$$\text{Answer } 0.497 \pm .007 (\pm 1.4\%)$$

3-19. (a) Show that the formula mass of NaCl is 58.4425 (+/- 0.0009) g/mol.

$$\text{Na} = 22.989770 \pm 0.000002 \text{ g/mol}$$

$$\text{Cl} = 35.4527 \pm 0.0009 \text{ g/mol}$$

$$\text{NaCl } 58.442470 \pm \sqrt{(2 \times 10^{-6})^2 + (9 \times 10^{-4})^2} = 9 \times 10^{-4}$$

$$\text{MW} = 58.4425 \pm 0.0009 \text{ g/mol}$$

(b) To prepare a solution of NaCl, you weigh out 2.634 (± 0.002) g and dissolve it in a volumetric flask whose volume is 100.00 (± 0.08) mL. Express the molarity of the solution, along with its uncertainty, with an appropriate number of digits.

$$2.634 (\pm 0.002) \text{ g NaCl} \times \frac{1 \text{ mol NaCl}}{58.4425 \pm 0.0009 \text{ g NaCl}} \times \frac{1}{0.10000 \pm 0.00008 \text{ L}} = 0.4507$$

uncertainties as percents

$$\sqrt{(0.07593\%)^2 + (0.00154\%)^2 + (0.08\%)^2} = \sqrt{0.012168} = 0.1103\%$$

$$0.4507 \times \pm 0.1103\% = 0.4507 \pm 0.000496 = 0.4507 \pm 0.0005 \text{ M}$$

4-2. Use Table 4-1 to state what fraction of a Gaussian population lies within the following intervals:

a) $\mu \pm \sigma$ area from 0 to $z = +1$ is 0.3413

area from $z = -1$ to 0 is 0.3413

sum is 0.6426

b) $\mu \pm 2\sigma$ area from 0 to $z = +2$ is 0.4773 twice this is 0.9546

c) μ to $+\sigma$ area = 0.3413

d) μ to $+0.5\sigma$ area = 0.1915

e) $-\sigma$ to -0.5σ area = $0.3413 - 0.1915 = 0.1498$

4-3. The ratio of the numbers of atoms of the isotopes of ^{69}Ga and ^{71}Ga in eight samples from different sources was measured in an effort to understand differences in reported values of the atomic mass of gallium: The eight values of $^{69}\text{Ga}/^{71}\text{Ga}$ are:

1.52660, 1.52974, 1.52592, 1.52731, 1.52894, 1.52804, 1.52685, 1.52793

Find the (a) mean, (b) standard deviation, and (c) variance.

(a) Mean = $1/8 (1.52660 + 1.52974 + 1.52592 + 1.52731 + 1.52894 + 1.52804 + 1.52685 + 1.52793) = 1.52767$ or we can do this on a calculator

(b) Standard deviation = $s = 0.00126$

(c) Variance = $s^2 = (0.00126)^2 = 1.59 \times 10^{-6}$

4-11. The percentage of an additive in gasoline was measured six times with the following results: 0.13, 0.12, 0.16, 0.17, 0.20, 0.11%. Find the 90% and 99% confidence intervals for the percentage of the additive.

We are asked to find confidence intervals. This is section 4-2 in the text starting on page 66. A confidence interval is given by equation 4-6 and can be calculated by the method used in the example at the bottom of page 66.

The equation is $\mu = \bar{x} \pm (t \cdot s) / \sqrt{n}$

First we need the mean and standard deviation. Learn to use your calculator or Excel to get these values. You should get $\bar{x} = 0.148$ and $s = 0.034$

Since we have 6 values, the degrees of freedom is $N - 1 = 6 - 1 = 5$. We get the values of t from Table 4-2. For a 90% confidence level, $t = 2.015$. For 99% $t = 4.604$.

90% confidence: $\mu = 0.148 \pm (2.015 \times 0.034) / \sqrt{6} = 0.148 \pm 0.028 = 0.15 \pm 0.03$ correct sig figs

99% confidence: $\mu = 0.148 \pm (4.604)(0.034) / \sqrt{6} = 0.148 \pm 0.056 = 0.15 \pm 0.06$ correct sig figs

We see that if we want to be 99% confident that the true value lies close to our experimental mean \bar{x} , that we need a confidence interval that is twice as large as at 90% confidence.

4-22. Using the Q test, decide whether the value 216 should be rejected from the set of results 192, 216, 202, 195, and 204.

To apply the Q test we arrange the data in order of increasing value and calculate the range and gap for the odd point. 192 195 202 204 216

$Q = \text{gap} / \text{range} = (216 - 204) / (216 - 192) = 0.50$ which is < 0.64 , the value from Table 4-6 for 5 observations.

Thus at the 90% confidence level we should retain the value 216. There is more than a 10% chance that the value is a member of the same population as the other four observations.