Chem 321 Lecture 11 - Chemical Activities

10/3/13

Student Learning Objectives

One of the assumptions that has been made in equilibrium calculations thus far has been to equate K to a ratio of concentrations. Such a K (sometimes referred to as a concentration equilibrium constant and given the symbol K′) is not constant. Look at data for the K′ values for three different reactions as the concentration of NaCl in the each solution is changed (Fig. 8.1). As the electrolyte concentration increases, K′ increases and at very low electrolyte concentrations K′ approaches a limiting value. Why does K′ change with changing salt concentration?

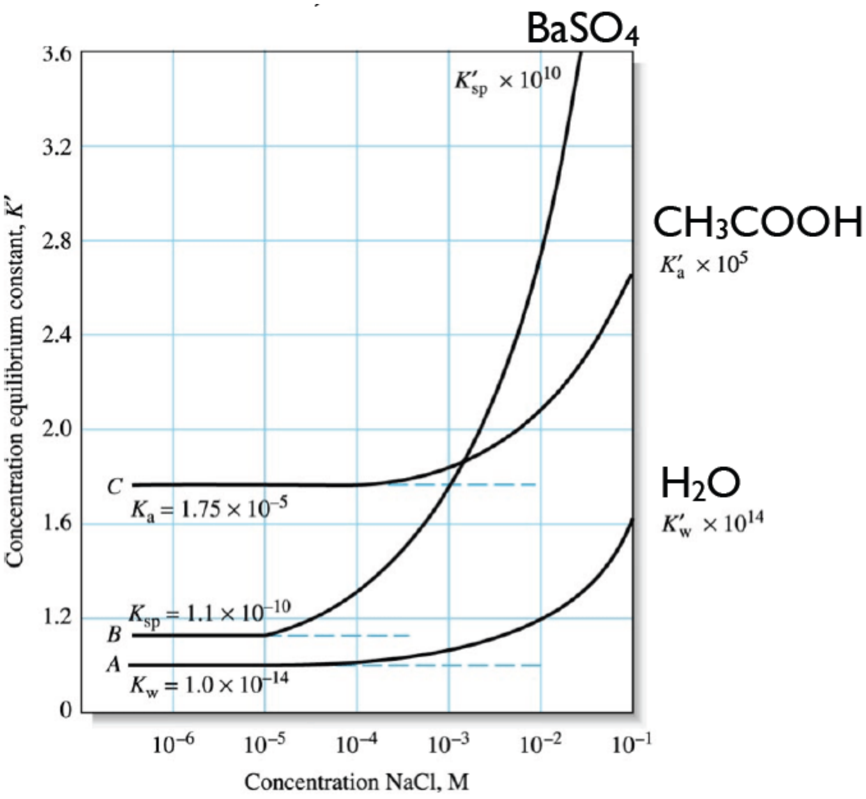

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Figure 8.1 Effect of electrolyte concentration on concentration-based equilibrium constants

Let's focus on one these reactions, the dissolution of $BaSO_4$.

$$BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq)$$

$$K'_{sp} = [Ba^{2+}][SO_4^{2-}]$$

The thermodynamic equilibrium constant (a true constant) for this or any other reaction is based on a ratio of chemical activities, not concentrations. For this reaction

$$K_{sp} = \frac{a_{Ba^{2+}} a_{SO_4^{2-}}}{a_{BaSO_4}} = a_{Ba^{2+}} a_{SO_4^{2-}}$$

The value of K_{sp} is the same as the limiting value when the electrolyte concentration is very low. This suggests that the activities depend on the salt concentration.

The **activity** of component A (a_A) can be calculated from the concentration of component A in solution ([A]) and its **activity coefficient (γ_A)** by

$$\mathbf{a_A = [A]\,\gamma_A}$$

Thus,

$$K_{sp} = a_{Ba^{2+}} a_{SO_4^{2-}} = [Ba^{2+}]\gamma_{Ba^{2+}}[SO_4^{2-}]\gamma_{SO_4^{2-}}$$

and

$$K'_{sp} = [Ba^{2+}][SO_4^{2-}] = \frac{K_{sp}}{\gamma_{Ba^{2+}}\gamma_{SO_4^{2-}}}$$

The reason K′ changes with the salt concentration is that the activity coefficients depend on the concentration of the salt. In 1923 Peter Debye and Erich Hückel developed an expression that allows one to calculate activity coefficients. The extended Debeye-Hückel equation indicates that γ depends on three factors.

$$-\log \gamma = \frac{0.51\, z^2 \sqrt{\mu}}{1 + (\alpha \sqrt{\mu}/305)}$$

where z is the charge on the ion;

α is the hydrated ion radius (in pm);

μ is the ionic strength of the solution.

The **ionic strength** of a solution is a measure of electrolyte concentration and is calculated by:

$$\mu = \frac{1}{2} \sum c_i z_i^2$$

where c is the molarity of a particular ion and z is the charge on the ion. This is the reason why K′ depends on the electrolyte concentration.

A close look at the Debeye-Hückel equation shows that γ decreases as the ion charge increases, the hydrated ionic radius decreases and as the ionic strength of the solution increases. The effect of ionic strength on the activity coefficient strongly depends on the charge of the ion (see Fig. 8.2).

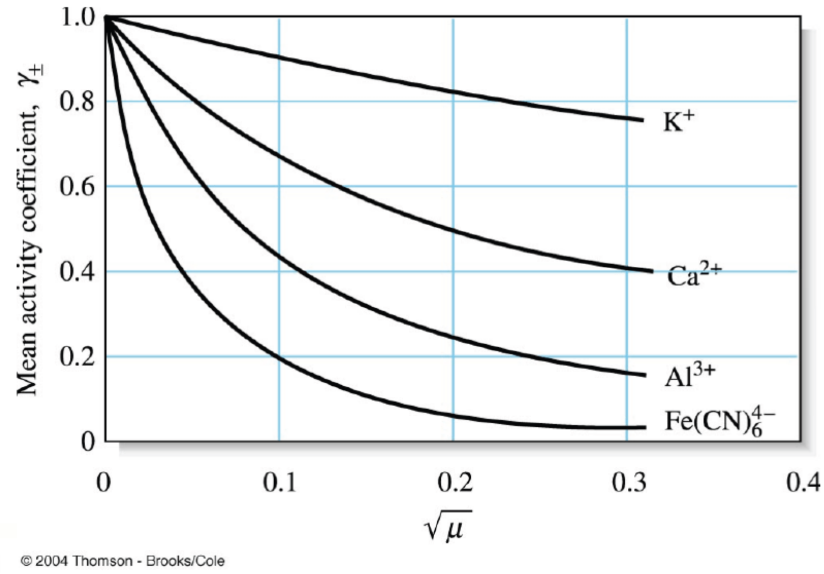


Figure 8.2 Effect of ionic strength on activity coefficients

The difference between the activity of solute ion A^n (a_A) and its formal concentration ($[A^n]$) arises because of ionic interactions between mobile ions in a solution. Individual ions in solution are surrounded by ions of opposite charge (they are shielded). Consequently, the formal charge an ion projects to other ions is less than it normally would be, so it interacts with oppositely-charged ions less attractively - its effective concentration is lower. The activity coefficient is a measure of how effectively an ion can interact in solution. In dilute solutions ($\mu < 0.1$ M), γ varies from 0 to 1. As the solution becomes more dilute (fewer ionic interactions), $\gamma \rightarrow 1$ and $a_A \rightarrow [A^n]$. For neutral solutes $\gamma = 1$.

Example 8.1

Problem

Calculate the ionic strength of a 0.060 M solution of KCl.

Solution

First, determine what ions are present in solution: K^+, Cl^-, H_3O^+, OH^-

Only those ions present in the higher concentrations ($[K^+] = [Cl^-] = 0.060$ M vs. $[H_3O^+] \sim [OH^-] \sim 10^{-7}$ M) need to be considered when calculating the ionic strength

$$\mu = \frac{1}{2}[(0.060\,M)(+1)^2 + (0.060\,M)(-1)^2] = 0.060\,M$$

Notice that the ionic strength is the same as the molarity of the (KCl) electrolyte. This is a general rule; whenever the electrolyte involves only ions with +1 and -1 charges the ionic strength is the same as the electrolyte concentration. This will not be the case when the electrolyte ions have larger charges.

Check for Understanding 8.1

Solution

1. What is the ionic strength of a 0.020 M Na_2SO_4 solution?

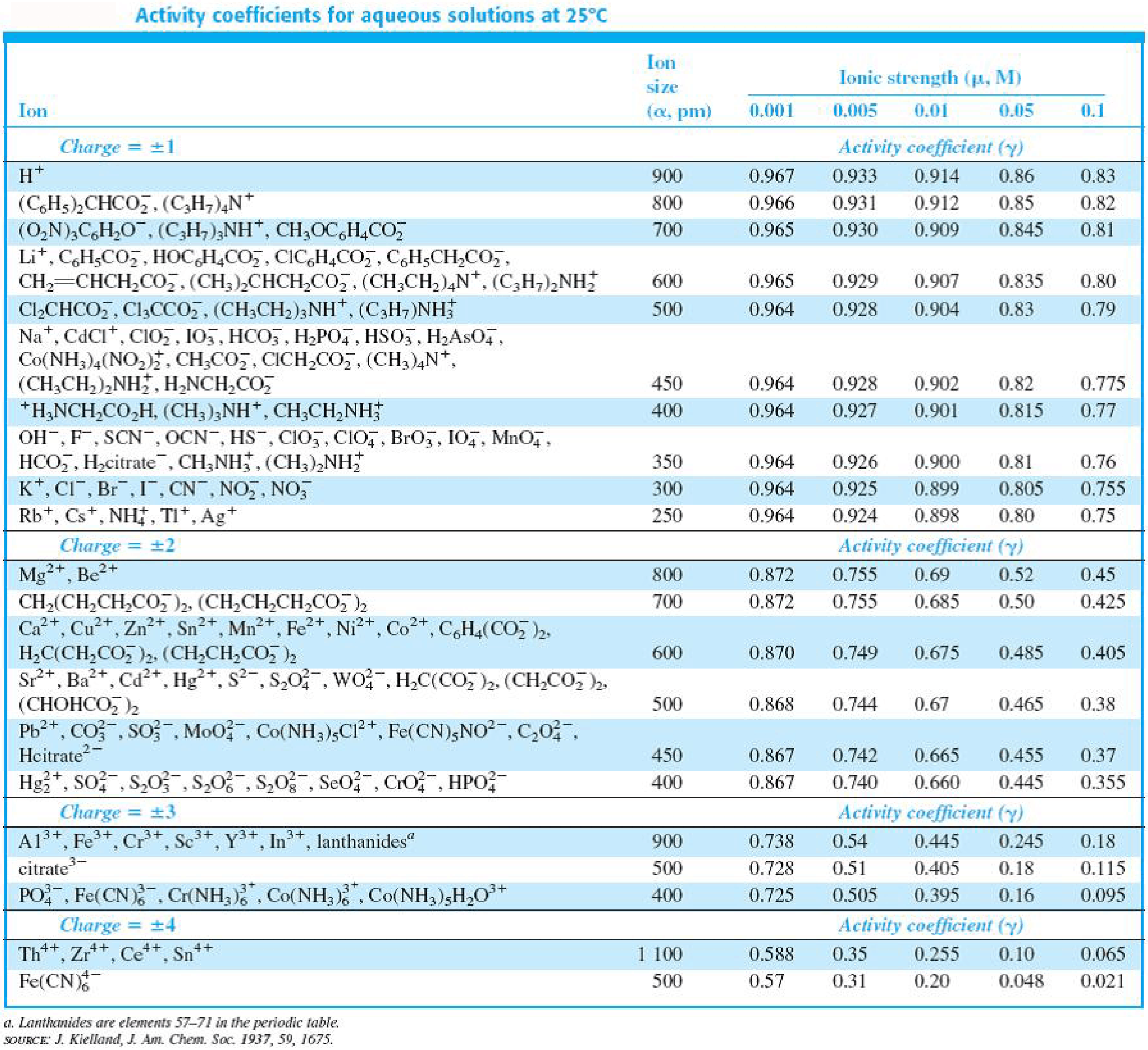
Another assumption that has been made so far in the acid-base equilibrium calculations is related to pH. The pH measurements in the laboratory are a measure of the activity of the hydrogen ion (a_{H+}), not its formal concentration. The proper relationship is

$$\mathbf{pH = -\log a_{H+}}$$

In some equliibrium calculations you will be able to determine a_{H+} directly, however, often you will first obtain the equilibrium $[H^+]$. Then you must multiply this by the appropriate activity coefficient to get a_{H+} before calculating the pH. Also note that

$$\mathbf{K_w = a_{H+}a_{OH-} = [H^+]\gamma_{H+}[OH^-]\gamma_{OH-}}$$

Generally, the activity coefficient of an ion will not be calculated. Instead, it will be gotten from a table of activity coefficients such as shown below, which lists γ as a function of ion charge, ion size and ionic strength. Note that γ does not depend on the specific nature of the electrolyte.



Activity coefficients for aqueous solutions at 25°C

Ion	Ion size (α, pm)	Ionic strength (μ, M)				
		0.001	0.005	0.01	0.05	0.1
Charge = ±1		*Activity coefficient (γ)*				
H^+	900	0.967	0.933	0.914	0.86	0.83
$(C_6H_5)_2CHCO_2^-$, $(C_3H_7)_4N^+$	800	0.966	0.931	0.912	0.85	0.82
$(O_2N)_3C_6H_2O^-$, $(C_3H_7)_3NH^+$, $CH_3OC_6H_4CO_2^-$	700	0.965	0.930	0.909	0.845	0.81
Li^+, $C_6H_5CO_2^-$, $HOC_6H_4CO_2^-$, $ClC_6H_4CO_2^-$, $C_6H_5CH_2CO_2^-$, $CH_2{=}CHCH_2CO_2^-$, $(CH_3)_2CHCH_2CO_2^-$, $(CH_3CH_2)_4N^+$, $(C_3H_7)_2NH_2^+$	600	0.965	0.929	0.907	0.835	0.80
$Cl_2CHCO_2^-$, $Cl_3CCO_2^-$, $(CH_3CH_2)_3NH^+$, $(C_3H_7)NH_3^+$	500	0.964	0.928	0.904	0.83	0.79
Na^+, $CdCl^+$, ClO_2^-, IO_3^-, HCO_3^-, $H_2PO_4^-$, HSO_3^-, $H_2AsO_4^-$, $Co(NH_3)_4(NO_2)_2^+$, $CH_3CO_2^-$, $ClCH_2CO_2^-$, $(CH_3)_4N^+$, $(CH_3CH_2)_2NH_2^+$, $H_2NCH_2CO_2^-$	450	0.964	0.928	0.902	0.82	0.775
$^+H_3NCH_2CO_2H$, $(CH_3)_3NH^+$, $CH_3CH_2NH_3^+$	400	0.964	0.927	0.901	0.815	0.77
OH^-, F^-, SCN^-, OCN^-, HS^-, ClO_3^-, ClO_4^-, BrO_3^-, IO_4^-, MnO_4^-, HCO_2^-, $H_2citrate^-$, $CH_3NH_3^+$, $(CH_3)_2NH_2^+$	350	0.964	0.926	0.900	0.81	0.76
K^+, Cl^-, Br^-, I^-, CN^-, NO_2^-, NO_3^-	300	0.964	0.925	0.899	0.805	0.755
Rb^+, Cs^+, NH_4^+, Tl^+, Ag^+	250	0.964	0.924	0.898	0.80	0.75
Charge = ±2		*Activity coefficient (γ)*				
Mg^{2+}, Be^{2+}	800	0.872	0.755	0.69	0.52	0.45
$CH_2(CH_2CH_2CO_2^-)_2$, $(CH_2CH_2CH_2CO_2^-)_2$	700	0.872	0.755	0.685	0.50	0.425
Ca^{2+}, Cu^{2+}, Zn^{2+}, Sn^{2+}, Mn^{2+}, Fe^{2+}, Ni^{2+}, Co^{2+}, $C_6H_4(CO_2^-)_2$, $H_2C(CH_2CO_2^-)_2$, $(CH_2CH_2CO_2^-)_2$	600	0.870	0.749	0.675	0.485	0.405
Sr^{2+}, Ba^{2+}, Cd^{2+}, Hg^{2+}, S^{2-}, $S_2O_4^{2-}$, WO_4^{2-}, $H_2C(CO_2^-)_2$, $(CH_2CO_2^-)_2$, $(CHOHCO_2^-)_2$	500	0.868	0.744	0.67	0.465	0.38
Pb^{2+}, CO_3^{2-}, SO_3^{2-}, MoO_4^{2-}, $Co(NH_3)_5Cl^{2+}$, $Fe(CN)_5NO^{2-}$, $C_2O_4^{2-}$, $Hcitrate^{2-}$	450	0.867	0.742	0.665	0.455	0.37
Hg_2^{2+}, SO_4^{2-}, $S_2O_3^{2-}$, $S_2O_6^{2-}$, $S_2O_8^{2-}$, SeO_4^{2-}, CrO_4^{2-}, HPO_4^{2-}	400	0.867	0.740	0.660	0.445	0.355
Charge = ±3		*Activity coefficient (γ)*				
$A1^{3+}$, Fe^{3+}, Cr^{3+}, Sc^{3+}, Y^{3+}, In^{3+}, lanthanides[a]	900	0.738	0.54	0.445	0.245	0.18
$citrate^{3-}$	500	0.728	0.51	0.405	0.18	0.115
PO_4^{3-}, $Fe(CN)_6^{3-}$, $Cr(NH_3)_6^{3+}$, $Co(NH_3)_6^{3+}$, $Co(NH_3)_5H_2O^{3+}$	400	0.725	0.505	0.395	0.16	0.095
Charge = ±4		*Activity coefficient (γ)*				
Th^{4+}, Zr^{4+}, Ce^{4+}, Sn^{4+}	1 100	0.588	0.35	0.255	0.10	0.065
$Fe(CN)_6^{4-}$	500	0.57	0.31	0.20	0.048	0.021

a. Lanthanides are elements 57–71 in the periodic table.

SOURCE: J. Kielland, J. Am. Chem. Soc. 1937, 59, 1675.

In order to take the ionic interactions into account when doing equilibrium calculations, the following general method will be used.

- First, write the reaction quotient in terms of activities (not concentrations) and set it equal to K.
- Substitute for each solute activity the product of activity coefficient times concentration. For pure solids and liquids, the activity is unity and for gases at a pressure of about 1 atm, the activity is approximated by the partial pressure.
- Determine the ionic strength of the solution and use this to get the needed activity coefficients from the data table. For uncharged solutes these ionic interactions are not very significant so $\gamma \sim 1$, independent of ionic strength.
- Set up the usual table of initial and equilibrium concentrations.
- Substitute the values for the concentration terms and activity coefficients into the reaction quotient and solve for the unknown term.
- If pH is to be determined, get $[H_3O^+]$ from the calculations described above, then calculate a_{H+} using the appropriate value for γ_{H+}. pH = $-\log a_{H+} = -\log ([H_3O^+]\gamma_{H+})$.

This method will be illustrated by using activities for the equilibrium calculation done in Example 8.2.

Example 8.2

Problem

Using activities, calculate the pH of a 0.10 M aqueous solution of KH_2PO_4.

Solution

First determine what ions are in solution. The only important ions in terms of ionic strength are those from the salt because their concentrations are much higher than the those for H^+ and OH^-. Since the electrolyte involves only +1 and -1 ions (K^+ and $H_2PO_4^-$), the ionic strength equals the electrolyte concentration (μ = 0.10 M). The needed activity coefficients can be gotten directly from the data table of activity coefficients for this ionic strength.

for μ = 0.10 M, $\gamma_{H3O+} = 0.83$

$\gamma_{HPO42-} = 0.355$

$\gamma_{H2PO4-} = 0.775$

The concentration table associated with the weak acid dissociation reaction is the same as before.

	$H_2PO_4^-$	+	H_2O	$\overset{K_{a2}}{\rightleftharpoons}$	H_3O^+	+	HPO_4^{2-}
initial	0.10 M				~10^{-7} M		0
equil	0.10 - x				10^{-7} + x ~ x		x

where x equals the increase in the $[HPO_4^{2-}]$. The equilibrium concentration of H_3O^+ is also approximated by x. This assumes that x >> 10^{-7} M.

Next write the reaction quotient in terms of activities and set it equal to K_a.

$$K_a = \frac{a_{H_3O^+}\, a_{HPO_4^{2-}}}{a_{H_2PO_4^-}\, a_{H_2O}} = \frac{[H_3O^+]\gamma_{H_3O^+}[HPO_4^{2-}]\gamma_{HPO_4^{2-}}}{[H_2PO_4^-]\gamma_{H_2PO_4^-}(1)}$$

Example 8.2 (continued)

Solution

Now substitute the various values for the quantities in the reaction quotient and solve for x.

$$K_a = 6.3\,x\,10^{-8} = \frac{[H_3O^+]\gamma_{H_3O^+}[HPO_4^{2-}]\gamma_{HPO_4^{2-}}}{[H_2PO_4^-]\gamma_{H_2PO_4^-}} = \frac{(x)(0.83)(x)(0.355)}{(0.10-x)(0.775)} \simeq \frac{x^2(0.83)(0.355)}{(0.10)(0.775)}$$

Note that the approximation made in the denominator assumes that x << 0.10 M.

This gives x = 1.2_9 x 10^{-4} M and validates the two assumptions that were made.

Thus, $[H_3O^+]$ = 1.2_9 x 10^{-4} M and a_{H3O+} = (1.2_9 x 10^{-4})(0.83) = 1.0_7 x 10^{-4}. Hence, pH = -log a_{H3O+} = 3.97.

Although the calculated pH appears to be only sightly lower than that determined before (4.10), note that the calculated equilibrium $[H_3O^+]$ is actually 60% higher than that gotten by ignoring ionic interactions. This suggests that the weak acid is ionized to a greater extent than previously expected. This makes sense in light of these ionic interactions. In the presence of electrolyte, the H_3O^+ and HPO_4^{2-} products are shielded from one another and are not able to recombine as readily.

In Example 8.2 the ionic strength of the solution (μ = 0.10 M) corresponded to one of the values listed in the table of activity coefficients. However, often this is not the case. In such a situation one must do a linear interpolation to obtain the desired activity coefficients.

Suppose, for example, you require the activity coefficient for a solution that has an ionic strength of 0.007 M. In the table of activity coefficients you are given the value of γ_{H3O+} for μ = 0.005 M and μ = 0.010 M. The desired value must fall between these . This situation is described in Figure 8.3.

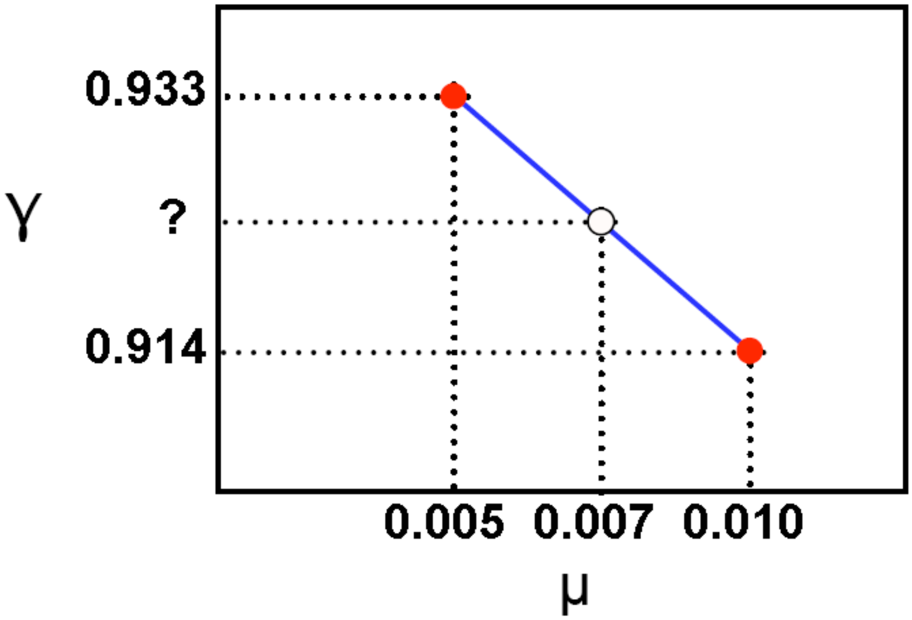


Figure 8.3 Linear interpolation to obtain activity coefficients

Another way of thinking about this is to use the following type of table.

μ	γ_{H3O+}
0.005	**0.933**
0.007	**x**
0.010	**0.914**

Then set up a proportion in the form

$$\frac{0.933 - x}{0.933 - 0.914} = \frac{0.007 - 0.005}{0.010 - 0.005}$$

and solve for x.

$$x = 0.933 - \frac{0.007 - 0.005}{.010 - 0.005}(0.933 - 0.914) = 0.925$$

Example 8.3

Problem

Using activities, calculate the pH of a solution made from mixing 100. mL of 0.030 M KH_2PO_4 with 100. mL of 0.050 M K_2HPO_4.

Solution

For the calculation of ionic strength, the important ions are: K^+, $H_2PO_4^-$ and HPO_4^{2-}.

from KH_2PO_4: $[K^+] = 0.015$ M
$[H_2PO_4^-] = 0.015$ M

Note that all concentrations are halved because of dilution.

from K_2HPO_4: $[K^+] = 0.050$ M
$[HPO_4^{2-}] = 0.025$ M

$$\mu = \frac{1}{2}[(0.015\,M)(+1)^2 + (0.015\,M)(-1)^2 + (0.050\,M)(+1)^2 + (0.025\,M)(-2)^2] = 0.090\,M$$

Since this ionic strength is not listed in the data table, the activity coefficients must be obtained by linear interpolation of the table data.

for μ = 0.090 M

$$\gamma_{H_3O^+} = 0.86 - \frac{0.090 - 0.050}{0.10 - 0.050}(0.86 - 0.83) = 0.83_6$$

$$\gamma_{H_2PO_4^-} = 0.82 - \frac{0.090 - 0.050}{0.10 - 0.050}(0.82 - 0.775) = 0.78_4$$

$$\gamma_{HPO_4^{2-}} = 0.445 - \frac{0.090 - 0.050}{0.10 - 0.050}(0.445 - 0.355) = 0.373$$

Example 8.3 (continued)

Solution

The concentration table for this buffer is the same as in Example 7.2.

	$H_2PO_4^-$	+	H_2O	$\overset{K_{a2}}{\rightleftharpoons}$	H_3O^+	+	HPO_4^{2-}
initial	0.015 M				$\sim 10^{-7}$ M		0.025 M
equil	~0.015 M				x		~0.025 M

Note that x is defined as the equilibrium concentration of H_3O^+.

Now substitute the various values for the quantities in the reaction quotient and solve for x.

$$K_a = 6.3 \, x \, 10^{-8} = \frac{[H_3O^+]\gamma_{H_3O^+}[HPO_4^{2-}]\gamma_{HPO_4^{2-}}}{[H_2PO_4^-]\gamma_{H_2PO_4^-}} = \frac{(x)(0.83_6)(0.025)(0.373)}{(0.015)(0.78_4)}$$

Solving this gives x = $9.5_0 \times 10^{-8}$ M = $[H_3O^+]$. This $[H_3O^+]$ is more than 2.5 times larger than that gotten by ignoring ionic interactions.

To get the buffer pH, $a_{H3O+} = (9.5_0 \times 10^{-8})(0.83_6) = 7.9_4 \times 10^{-8}$. Hence, pH = -log a_{H3O+} = 7.10. This is a decidedly different pH than calculated before (7.42).

Check for Understanding 8.2

Solution

1. In Example 8.3 why can the $[H_3O^+]$ and $[OH^-]$ be ignored when calculating the buffer solution ionic strength?

Exercises for Chemical Activities