CONCEPT: ACTIVITY COEFFICIENTS

In order to express the effect of ionic strength on the concentration of species we calculate its activity with the use of an *activity coefficient*, which is given in units of gamma.

$$A_C = [C]\gamma_C \qquad \begin{aligned} A_C &= \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ \text{ of the compound} \\ [C] &= \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ \text{ of the compound} \\ \gamma_C &= \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ \text{ of the compound} \end{aligned}$$

The activity coefficient and ionic strength can be more closely and accurately related by using the extended Debye-Huckel equation:

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

The effect of ionic strength, ionic charge and ionic size on the activity coefficient:

1. As ionic strength ____ , the activity coefficient will ____ and as the activity coefficient approaches ____ , ionic strength approaches ____.
2. As the size of ionic charge ____ , the more activity coefficient moves away from unity.
3. The smaller the ionic size ____ , the greater the effects of the activity coefficient.

EXAMPLE 1: For the following compound, state the solubility product expression with its acticity coefficient.

$Cu_2(PO_4)_3$

EXAMPLE 2: For the following compound, state the solubility product expression with its acticity coefficient.

Mo_2S_5

<u>**CONCEPT:** ACTIVITY COEFFICIENT TABLE</u>

By calculating the ionic strength of a compound the activity coefficient can be determined by the chart given below.

Activity Coefficients

	Ionic Size	Ionic Strength (μ, M)				
Ions	(α, pm)	0.001	0.005	0.01	0.05	0.1
Charges = ±1		**Activity Coefficients (γ)**				
H^+	900	0.967	0.933	0.914	0.860	0.830
$(C_6H_5)_2CHCO_2^-$, $(C_3H_7)_4N^+$	800	0.966	0.931	0.912	0.850	0.820
$(O_2N)_3C_6H_2O^-$, $(C_3H_7)_3NH^+$, $CH_3OC_6H_4CO_2^-$	700	0.965	0.930	0.909	0.845	0.810
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	0.800
$Cl_2CHCO_2^-$, $Cl_3CCO_2^-$, $(CH_3CH_2)_3NH^+$, $(C_3H_7)NH_3^+$	500	0.964	0.928	0.904	0.830	0.790
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	0.820	0.775
$^+H_3NCH_2CO_2H$, $(CH_3)_3NH^+$, $CH_3CH_2NH_3^+$	400	0.964	0.927	0.901	0.815	0.770
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	0.810	0.760
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	0.800	0.750
Charges = ±2		**Activity Coefficients (γ)**				
Mg^{2+}, Be^{2+}	800	0.872	0.755	0.690	0.520	0.450
$CH_2(CH_2CH_2CO_2^-)_2$, $(CH_2CH_2CH_2CO_2^-)_2$	700	0.872	0.755	0.685	0.500	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	0.670	0.465	0.380
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	0.370
Hg^{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
Charges = ±3		**Activity Coefficients (γ)**				
Al^{3+}, Fe^{3+}, Cr^{3+}, Sc^{3+}, Y^{3+}, In^{3+}, lanthanides[a]	900	0.738	0.540	0.445	0.245	0.180
$citrate^{3-}$	500	0.728	0.510	0.405	0.180	0.115
PO_4^{3-}, $Fe(CN)_6^{3-}$, $Cr(NH_3)_6^{3+}$, $Co(NH_3)_3^{3+}$, $Co(NH_3)_5H_2O^{3+}$	400	0.725	0.505	0.395	0.160	0.095
Charges = ±4		**Activity Coefficients (γ)**				
Th^{4+}, Zr^{4+}, Ce^{4+}, Sn^{4+}	1100	0.588	0.350	0.255	0.100	0.065
$Fe(CN)_6^{4-}$	500	0.570	0.310	0.200	0.048	0.021

EXAMPLE: Find the activity coefficient for the ion specified in the following compound:

a) Na^+ in 0.005 M NaCl

CONCEPT: ACTIVITY COEFFICIENT TABLE CALCULATIONS 1

EXAMPLE 1: Find the activity coefficient for the ion specified in the following compound:

CN^- in 1.0 mM RbCN

EXAMPLE 2: Find the activity coefficient for the ion specified in the following compound:

Zr^{4+} in 5.0 mM $Zr(NO_3)_4$

PRACTICE: Calculate the activity coefficient of H^+ using the extended Debye-Huckel equation for a solution comprised of H^+ and I^-. Given that H^+ has a size of 9.00 x 10^{-10} m and the molar concentration of the solution is 0.075.

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

CONCEPT: NON-IDEAL IONIC STRENGTH

Sometimes the ionic strength of a dissolvable compound you calculate may not be found on your chart.

- In a case like this you can just use ______________________ to find the best answer for our activity coefficient.

$$\frac{\text{Unknown } \gamma \text{ interval}}{\Delta\gamma} = \frac{\text{known } \mu \text{ interval}}{\Delta\mu}$$

EXAMPLE: Find the activity coefficient from the given ionic strength, μ, for the following ion.

Ba^{2+} when $\mu = 0.075$

Ions	Ionic Size (α, pm)	Ionic Strength (μ, M)				
		0.001	0.005	0.01	0.05	0.1
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	0.670	0.465	0.380

PRACTICE: Find the activity coefficient from the given ionic strength, μ, for the following ion.

F^- when $\mu = 0.0080$

Ions	Ionic Size (α, pm)	Ionic Strength (μ, M)				
		0.001	0.005	0.01	0.05	0.1
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	0.810	0.760