Chapter 8 – Activity continued

$$a\,A + b\,B = c\,C + d\,D$$

Reactants **Products**

$$K = [C]^c[D]^d / [A]^a[B]^b$$

BUT REALLY….

$$K = \mathcal{A}_c^{\,c}\ \mathcal{A}_d^{\,d} / \mathcal{A}_a^{\,a}\ \mathcal{A}_b^{\,b}$$

or

$$K = [C]^c \gamma_c^{\,c}\ [D]^d \gamma_d^{\,d} / [A]^a \gamma_a^{\,a}\ [B]^b \gamma_b^{\,b}$$

Activity: $\mathcal{A} = [X]^x \gamma_x^{\,x}$

We know [X] is the molar concentration (moles/L).

γ_x is the activity coefficient for species X.

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

Where: $\mu = 0.5\, \Sigma\, c_i\, z_i^2$ (ionic strength)

(c_i = molarity of ith ion and z_i = charge on ith ion)

z = charge of species x

α = ionic size (pm)

Table 8-1

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						
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

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

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

Points concerning Activity ($\mathcal{A}$):

- Concentration of ions (ionic strength, μ) is important.
- Charge on ions (z) is important.
- Size of ions (α) is important.
- “Activity” ($\mathcal{A}$) should be used for exact work.
- The activity coefficient **(γ_x)**of a species is a measure of the effectiveness with which that species influences an equilibrium.
- In very dilute solutions (μis small), this effectiveness becomes constant and the activity coefficient is unity. The activity and molar conc. of the species is equal.

Problem 1 – Ionic Strength Calculation

Assuming complete dissociation of the salts, calculate the ionic strength, μ, of the following:

a) 0.2 mM KNO_3

b) 0.2 mM Cs_2CrO_4

Problem 2 – Activity coefficient calculation

What is the activity coeffiecient, γ, for the following:

a) Al^{3+} when $\mu = 0.05$ M.

b) Al^{3+} when $\mu = 0.003$ M.

Problem 3 – Using activities for solubility problems.

Using activities, find the solubility of AgSCN (moles of Ag^{+} / L in the following:

a) In a solution of 0.060 M KNO_3.

b) In a solution of 0.060 KSCN.