

Understanding Solubility: Preparing Spreadsheets & Graphs with Excel

Adapted from: J Chem Ed, Vol. 78, p.268, February 2001, On-Line Supplement, Pamela Brown, Ph.D., PE, Chemical Technology Program, New York City Technical College, Brooklyn, NY 11201

Learning Objectives:

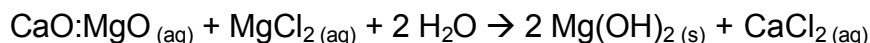
1. Understand the thermodynamic relationship of solubility/ K_{sp} and entropy/enthalpy.
2. Develop skills in Microsoft Excel to prepare tables, figures and graphs.
3. Apply linear curve-fitting to data using Excel.
4. Apply acquired knowledge and skills to experimental data for barium iodate.

Background:

Solubility is a measure of how much of a material, the solute, dissolves in a solvent. Materials are generally characterized as soluble, slightly soluble, and insoluble. Materials are considered insoluble if less than 0.01 M dissolves (1).

Solubility generally increases as the temperature increases. This can be understood in terms of LeChatelier's Principle - when a system at equilibrium is subjected to a change in temperature or pressure, the system will adjust itself to a new equilibrium to relieve the effects of the change. The enthalpy of solution is usually endothermic (energy is absorbed). Thus, an increase in temperature results in an increase in solubility. Some materials, especially carbonates, exhibit **reverse solubility**, i.e. the solubility decreases as the temperature increases. These materials have an exothermic enthalpy of solution. Distilled water is used in steam boilers because the magnesium and calcium ions which may be present in tap water will form insoluble carbonates, resulting in scaling (build-up of solids which are extremely difficult to remove) on boiler surfaces. Scaling causes a significant reduction in heat transfer and boiler efficiency. In distilled water, Ca^{2+} and Mg^{2+} ions are absent, so scaling is less of a problem.

Understanding solubility is important because it has so many implications in purification, corrosion, material compatibility, and pollution control. Dissolved materials change the freezing and boiling point of solutions, and may affect the electrical conductivity. Untreated tap water will cause pipes and fixtures to corrode, which may release copper, zinc, and lead into drinking water. To prevent corrosion, municipalities adjust the pH and add small quantities of orthophosphates. The orthophosphates create a protective layer on metal surfaces (2). Differences in solubility can be used to separate and purify materials. For example, magnesium is recovered from seawater by the precipitation of its hydroxide with lime (CaO) or calcined dolomite (CaO:MgO), as shown below (3):



Linear curve-fitting to estimate enthalpy and entropy changes

Development of the Thermodynamic Equations

Background:

Saturated aqueous solutions are in dynamic equilibrium with any undissolved solute. The relationship between the equilibrium constant, which is the solubility product, and the enthalpy change associated with dissolution is given by the van't Hoff equation:

$$\frac{d \ln K_{sp}}{dT} = \frac{\Delta H}{RT^2}$$

where K_{sp} is the solubility product, ΔH is the change in enthalpy per mole due to dissolution, and T is the temperature in degrees Kelvin.

If ΔH is constant, integration yields the **linear equation**:

$$\ln K_{sp} = \frac{-\Delta H}{RT} + C$$

It is referred to as the **linear equation** since it is the equation of a straight line of the form:

$$y = mx + b$$

where the values of y are $\ln K_{sp}$, and values of x are $1/T$. The slope, **m** = $-\Delta H/R$, and the **y-intercept**, **b**, is the constant C , which equals $\Delta S/R$.

Determining enthalpy (ΔH) and entropy (ΔS) changes from plots of $\ln K_{sp}$ vs T^{-1} (K^{-1})

Example 1: When the values of $\ln K_{sp}$ vs. $1/T(K)$ are plotted for $K_2Cr_2O_7$, the linear curve-fit equation which results is: $y = -7805.4x + 25.09$ (See Figure 2)

Calculate enthalpy and entropy change for the dissolution of $K_2Cr_2O_7$ in water.

Solution: From examination of the given linear curve-fit equation it can be seen that:

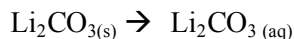
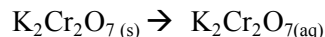
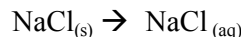
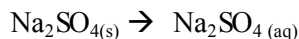
$$m = \frac{-\Delta H}{R} = -7805.4 \text{ K} ; b = \Delta S/R = 25.09 \text{ K}$$

$$\Delta H = (7805.4 \text{ K})(R) = (7805.4 \text{ K})(8.314 \text{ J}\cdot\text{mole}^{-1}\text{K}^{-1}) = 64894 \text{ J}\cdot\text{mole}^{-1} = 64.89 \text{ kJ}\cdot\text{mole}^{-1}$$

$$\Delta S = 25.09 \text{ K} (8.314 \text{ J}\cdot\text{mole}^{-1}\text{K}^{-1}) = 208.6 \text{ J}\cdot\text{mole}^{-1}$$

Enthalpies of solution from thermodynamic data

The enthalpy change associated with dissolution is related to the enthalpy of solution for each of the 5 salts. These reactions are:



Standard enthalpies and entropies of formation are presented in Table 4.

Table 4
Standard Enthalpies and Entropies of Formation

Substance	ΔH_f° (kJ-mole ⁻¹)	ΔS_f° (J-mole ⁻¹)
H ₂ O _(l)	-285.830	
K ₂ Cr ₂ O _{7(aq)}	-1994.5	466.9
K ₂ Cr ₂ O _{7(s)}	-2061.5	288.7
Ba (IO ₃) _{2(s)}	-1027.17	249.3
Ba (IO ₃) _{2(aq)}	-980.3	246.4
Ba (IO ₃) ₂ ·H ₂ O _(s)	-1322.14	297.1
Li ₂ CO _{3(aq)}	-1232.17	
Li ₂ CO _{3(s)}	-1215.9	
NaCl _(aq)	-407.27	
NaCl _(s)	-411.2	
Na ₂ SO _{4(aq)}	-1390.02	
Na ₂ SO ₄ ·10H ₂ O _(s)	-4327.26	
Na ₂ SO _{4(s)}	-1387.1	

The enthalpy or entropy of reaction, in this case the standard change of solution, ΔH_{sol}° or ΔS_{sol}° at standard conditions, is equal to the sum of the enthalpies or entropies of formation of the products minus the sum of the enthalpies or entropies of formation of the reactants:

$$\Delta H_{Rxn}^\circ = \sum \Delta H_{products}^\circ - \sum \Delta H_{reactants}^\circ$$

$$\Delta S_{Rxn}^\circ = \sum \Delta S_{products}^\circ - \sum \Delta S_{reactants}^\circ$$

Standard enthalpies and entropies of solution from standard enthalpies and entropies of formation

Example 2: Calculate the enthalpy and entropy of solution for K₂Cr₂O_{7(s)} using the standard enthalpies of formation in Table 4. Compare your result to the enthalpy of solution calculated in Example 1.

Solution:

$$\Delta H_{Rxn}^\circ = \sum \Delta H_{products}^\circ - \sum \Delta H_{reactants}^\circ = \Delta H_{K2Cr2O7(aq)}^\circ - \Delta H_{K2Cr2O7(s)}^\circ$$

$$= (-1994.58 \text{ kJ-mole}^{-1}) - (-2061.5 \text{ kJ-mole}^{-1}) = 66.9 \text{ kJ-mole}^{-1}$$

$$\Delta S_{Rxn}^\circ = \sum \Delta S_{products}^\circ - \sum \Delta S_{reactants}^\circ = \Delta S_{K2Cr2O7(aq)}^\circ - \Delta S_{K2Cr2O7(s)}^\circ$$

$$= (466.9 \text{ J-mole}^{-1}) - (288.7 \text{ J-mole}^{-1}) = 178.2 \text{ J-mole}^{-1}$$

The enthalpy change found in Example 1 was 64.9 kJ-mole⁻¹. It can be seen that there is fairly good agreement in enthalpy between the two methods (within 3%), and although there is a 16% difference between the methods in entropy, it is inconsequential since entropy is relatively small when compared to the enthalpy (0.2% difference). These differences can be attributed to interactions between the ions in solution, and temperature effects.

K_{sp} from Solubility Data

In order to calculate the solubility product, K_{sp} , the solubility data in units of **g solute/100 g water**, must be converted to molarity, in **moles/liter**. The density of the saturated solution is needed. Density data for saturated solutions of K₂Cr₂O₇, Na₂SO₄, and NaCl, are given in Table 5 (3, 4).

Table 5
Densities (g mL⁻¹ or g cm⁻³)

Temperature(C)	Na ₂ S O ₄ (sat'd sol.)	NaCl (sat'd sol.)	K ₂ Cr ₂ O ₇ (sat'd sol.)	Ba(IO ₃) ₂ (pure solid)	H ₂ O (pure liquid)
0	1.04	1.209			0.99987
10	1.08	1.204	1.06		0.99973
20	1.15	1.200	1.07		0.99823
25				4.998	0.99704
30	1.29	1.196			0.99567
40	1.32	1.191			0.99224
60	1.29	1.183			0.98324
80	1.27	1.175			0.97183
100	1.25	1.170			0.95838

A formula for converting the solubility to molarity is:

$$M = \left(\frac{g \text{ solute}}{g \text{ soln}} \right) \left(\text{density in } \frac{g \text{ soln}}{mL} \right) \left(\frac{1}{FM \text{ of solute in } \frac{g}{mole}} \right) \left(\frac{1000 \text{ mL}}{L} \right)$$

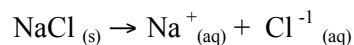
Converting solubility from units of g solute/100g water to Molarity (M)

Example 3 - Calculate the solubility in molarity, for NaCl at 0° C.

Solution - The solubility of NaCl at 0°C is 35.6 g NaCl /100 g H₂O. That means there are 35.6 g NaCl per (100 +35.6) g of solution. The solubility is thus equivalent to 35.6 g NaCl/135.6 g solution. This is converted to molarity by multiplying by the density of the saturated solution and converting the units of volume from milliliters to liters:

$$\left(\frac{35.6 \text{ g NaCl}}{135.6 \text{ g solution}} \right) \left(\frac{1.209 \text{ g}}{mL} \right) \left(\frac{1 \text{ mole NaCl}}{58.4 \text{ g NaCl}} \right) \left(\frac{1000 \text{ mL}}{L} \right) = 5.43 \text{ M NaCl}_{(aq)}$$

The equilibrium that is established when NaCl dissolves in water is:



The solubility-product equilibrium constant, K_{sp}, is given by:

$$K_{sp} = [\text{Na}^+_{(aq)}] [\text{Cl}^-_{(aq)}]$$

The concentrations of Na⁺ and Cl⁻ are the same, and equal to the saturation concentration, which is 5.43M NaCl.

Example 4 - Calculate the solubility product, K_{sp}, for NaCl at 0°C.

Solution - When one mole of NaCl dissolves, it produces one mole of $\text{Na}^+_{(\text{aq})}$ and one mole of $\text{Cl}^-_{(\text{aq})}$. In Example 4 it was determined that the saturation concentration of $\text{NaCl}_{(\text{aq})} = 5.43 \text{ M}$. Thus the concentrations of both $\text{Na}^+_{(\text{aq})}$ and $\text{Cl}^-_{(\text{aq})}$ are 5.43 M. The value of K_{sp} equals:

$$K_{\text{sp}} = [\text{Na}^+_{(\text{aq})}] [\text{Cl}^-_{(\text{aq})}] = (5.43\text{M})(5.43 \text{ M}) = 29.0$$

Examination of Table 5 shows that density data is not available for all saturated solutions at all temperatures. In these cases, pure component data can be used to estimate the density.

The formula for estimating the density is:

$$\text{density of saturated soln} = \frac{\text{mass of saturated soln}}{\frac{\text{solute mass}}{\text{solute density}} + \frac{\text{solvent mass}}{\text{solvent density}}}$$

Example 5- Calculate the molarity and solubility product, K_{sp} , for saturated $\text{K}_2\text{Cr}_2\text{O}_7$ at 30°C. The density of water at 30°C is 0.99567 g/mL. The density of solid $\text{K}_2\text{Cr}_2\text{O}_7$ is given in Table 3.

Solution- It is necessary to estimate the density using Eq. (22). Note that the solubility is 20 g $\text{K}_2\text{Cr}_2\text{O}_7 / 100 \text{ g H}_2\text{O}$, which means the total mass of the saturated solution is $(20 + 100) = 120 \text{ g}$.

$$\text{density of saturated } \text{K}_2\text{Cr}_2\text{O}_{7(\text{aq})} = \frac{120 \text{ g}}{\left(\frac{100 \text{ g H}_2\text{O}}{0.99567 \frac{\text{g}}{\text{mL}}} \right) + \left(\frac{20 \text{ g K}_2\text{Cr}_2\text{O}_7}{2.676 \frac{\text{g}}{\text{mL}}} \right)} = 1.11 \text{ g/mL}$$

Next, calculate the molarity of saturated $\text{K}_2\text{Cr}_2\text{O}_{7(\text{aq})}$:

$$M = \left(\frac{20 \text{ g K}_2\text{Cr}_2\text{O}_7}{120 \text{ g solution}} \right) \left(\frac{1.11 \text{ g}}{\text{ml}} \right) \left(\frac{1 \text{ mole K}_2\text{Cr}_2\text{O}_7}{294.19 \text{ g}} \right) \left(\frac{1000 \text{ mL}}{\text{L}} \right) = 0.63 \text{ M}$$

The equilibrium that is established when $\text{K}_2\text{Cr}_2\text{O}_7$ dissolves in water is:



The solubility-product equilibrium constant, K_{sp} , is given by :

$$K_{\text{sp}} = [\text{K}^+_{(\text{aq})}]^2 [\text{Cr}_2\text{O}_7^{2-}_{(\text{aq})}]$$

It can be seen that when one mole of $\text{K}_2\text{Cr}_2\text{O}_7$ dissolves, it produces two moles of $\text{K}^+_{(\text{aq})}$ and mole of $\text{Cr}_2\text{O}_7^{2-}_{(\text{aq})}$. Above it was determined that the concentration of saturated $\text{K}_2\text{Cr}_2\text{O}_{7(\text{aq})}$ is 0.630 M. Thus $[\text{K}^+_{(\text{aq})}] = (2)(0.630) = 1.260 \text{ M}$ and $[\text{Cr}_2\text{O}_7^{2-}_{(\text{aq})}] = 0.630 \text{ M}$. The value of K_{sp} equals:

$$K_{\text{sp}} = [\text{K}^+_{(\text{aq})}]^2 [\text{Cr}_2\text{O}_7^{2-}_{(\text{aq})}] = (1.260 \text{ M})^2 (0.630 \text{ M}) = 1.00$$

Calculated values of molarity, M and solubility product K_{sp} are summarized in Table 6.

Table 6
Solubility (M) and Solubility Product (Ksp) as a Function of Temperature (C)

Temp/C	Na ₂ SO ₄		K ₂ Cr ₂ O ₇		NaCl		Li ₂ CO ₃	
	Sol. (M)	K _{sp}	Sol. (M)	K _{sp}	Sol. (M)	K _{sp}	Sol. (M)	K _{sp}
0	0.335	0.151	0.167	.0189	5.43	29.5	.207	.0354
10	0.628	0.989	1.04	.0498	5.41	29.4	.192	.0283
20	1.32	9.10	1.07	.237	5.41	29.3	.179	.0227
30	2.63	72.9	1.11	1.00	5.43	29.5	.168	.0188
40	3.05	113.	1.14	2.05	5.44	29.6	.156	.0153
60	2.83	90.8	1.21	7.65	5.48	30.0	.134	.00972
80	2.72	80.4	1.28	18.0	5.55	318	.111	.00550
100	2.62	72.3	1.34	33.3	5.70	32.5	.0930	.00320