

## Lab 6: Using Thermodynamic Data to Predict Precipitation Reactions

Thermodynamic calculations allow us to calculate and predict whether a reaction will be spontaneous. In order to understand how we can perform such calculations and make a conclusion about spontaneity, we need to first understand a few thermodynamic functions.

Two state functions have been defined to describe the tendency for a reaction to occur spontaneously.

The first of these state functions is  $\Delta H$ , or the enthalpy change. Enthalpy changes that are negative are said to be exothermic, or releasing heat. Positive enthalpy changes are said to be endothermic, or requiring heat. In terms of spontaneity, spontaneous processes tend to be ones that are exothermic, or releasing of heat. Think about combustion for a moment – combustion releases heat, and it is a spontaneous reaction that once begun, continues until the reaction runs out of fuel (either oxygen or the combustible reagent). A change can still be spontaneous however, even when  $\Delta H$  is positive, or endothermic. An example of this would be melting of an ice cube at room temperature. It requires heat for an ice cube to melt, so  $\Delta H$  must be positive. Yet clearly the melting of an ice cube is spontaneous. So spontaneity may be affected by  $\Delta H$ , but  $\Delta H$  is not the only contributor in determining whether something is spontaneous or not.

The second state function that affects spontaneity is  $\Delta S$ , or entropy change. Entropy is the thermodynamic function that describes how systems tend toward homogeneity. In a practical sense, this can be thought of as systems tend to move from ordered states to more random or disordered states. It may seem strange that this is a quantifiable function, but it is readily quantifiable, and is critical in nearly every change that occurs. Think about the building you are sitting in right now. Entropy attempts to pull the building apart (this is effectively the 2<sup>nd</sup> law of thermodynamics: entropy happens). Entropy would pull your building apart and it would collapse if it were not for the bonds in the cement and wood that hold up the structure. If these bonds were to fail, the building would crumble to dust. This is increasing disorder, this is a positive  $\Delta S$ . Once the building has collapsed into dust, do you think it would ever reconstruct itself into a new building? Do things spontaneously impose order on themselves? This is what it means for entropy to drive a reaction forward.

In the previous example of a melting ice cube, the reason why the reaction is spontaneous, despite being endothermic, is that entropy is increasing. The molecules of water are moving from a rigid and ordered solid state, to a more fluid and disordered liquid state. Once in the liquid state, the molecules do not return to the solid state because it would require energy to impose that sort of order on the water molecules and regain their crystalline structure. Solid ice forms because bond formation is favorable from a  $\Delta H$  standpoint – forming bonds is always exothermic. However, forming a solid is bad from an entropic standpoint, because it requires overcoming disorder. What determines the break-point is temperature. At higher temperatures the molecules tend to shake themselves apart and become more disordered. In general: at higher temperatures, entropy wins.

A positive  $\Delta S$  tends to be spontaneous, a negative  $\Delta S$  tends to be nonspontaneous. Just like with  $\Delta H$  though, entropy alone is not sufficient to dictate whether a reaction is spontaneous or not.

There is an equation which puts both  $\Delta H$  and  $\Delta S$  together to determine overall spontaneity:

$$\text{Eq 1: } \quad \Delta G = \Delta H - T\Delta S$$

$\Delta G$  is known as Gibbs Free Energy. Based on the above description, it should be clear that a negative  $\Delta G$  is spontaneous. A negative  $\Delta H$  tends to make  $\Delta G$  negative (but alone is not sufficient to guarantee that  $\Delta G$  is negative). A positive  $\Delta S$  tends to make  $\Delta G$  negative. Thus a reaction that is exothermic (negative  $\Delta G$ ) and increasing in entropy (positive  $\Delta S$ ) will ALWAYS be spontaneous (negative  $\Delta G$ ).

So what we need to be able to do is calculate  $\Delta G$ , and there are a few ways to do this. The first is to use the free energies of formation to determine the  $\Delta G$  of a reaction. The equation for this is as follows:

$$\text{Eq 2: } \quad \Delta G^{\circ}_{298,\text{overall}} = \sum \Delta G^{\circ}_{f,298,\text{products}} - \sum \Delta G^{\circ}_{f,298,\text{reactants}}$$

This equation states that you can obtain the free energy change for any reaction by taking the sum of the free energies of formation of the products and subtracting from them the free energies of formation of the reactants (essentially how much energy do you get when you form the products, minus the energy it took to consume the reactants, is the overall energy change of a reaction). Most textbooks have these " $\Delta G^{\circ}_f$ " readily available, so one can readily calculate the  $\Delta G^{\circ}$  for millions of reactions. You'll be doing this calculation several times while filling out parts of Table 1.

$\Delta G^{\circ}_f$  is the standard free energy of formation for a compound. The "f" represents formation, and this means that you are forming 1 mole of the compound from its elements in their standard state. The degree symbol ( $^{\circ}$ ) means this is the value of  $\Delta G$  under standard conditions. This typically means normal atmospheric pressure, 1 molar concentration for solutions, 1 atm of pressure for gases, and pure quantities of any liquid or solid. If you deviate from these requirements, you are no longer under standard conditions. There must still be a  $\Delta G$  governing reactions under non-standard conditions, and we can determine the  $\Delta G$ -nonstandard using the following conversion:

$$\text{Eq 3: } \quad \Delta G = \Delta G^{\circ} + 2.303*RT\log(Q)$$

Equation 3 can also be written as  $\Delta G = \Delta G^{\circ} + RT\ln(Q)$  because  $\ln(x) = 2.303*\log(x)$ . ( $R = 8.314 \text{ J/molK}$ .) Essentially to use this equation you need to put in the correct value for  $T$  (temperature) and more importantly:  $Q$  (the reaction quotient). If you are under standard conditions, the value of  $Q$  will be 1 (1 Molar for everything in solution, 1 atm for gases, pure liquids and solids). The log of 1 is 0, so you get  $\Delta G = \Delta G^{\circ}$ .

But when you're not under standard concentrations,  $Q$  will not be 1, and thus it will affect the value of the free energy term accordingly.

Another way to calculate  $\Delta G^\circ$  is to simply use equation 1. The nice thing about equation 1 is that most textbooks, in addition to providing  $\Delta G^\circ_f$  values, also typically supply  $\Delta H^\circ_{298}$  and  $\Delta S^\circ_{298}$  values. One can calculate  $\Delta G^\circ$  for a compound by using the  $\Delta H^\circ_{298}$  and  $\Delta S^\circ_{298}$  values in the back of the book.

So why would someone use equation 1, when they could just use equation 2 to calculate a  $\Delta G^\circ$ ? The answer comes when you have to alter temperature. It turns out  $\Delta G^\circ$  changes a lot with temperature, and  $\Delta H^\circ$  and  $\Delta S^\circ$  do not. Because of this, if you are calculate  $\Delta G^\circ$  at temperatures other than 298K, you should use the following equation:

**Eq 4:**             $\Delta G_T = \Delta H_{298} - T\Delta S_{298}$

**Protocol:**

Complete **Table 1** below before beginning the experiment.

Use the thermodynamic data table on the following page to help you calculate and fill out Table 1.

- Write the salt/ppt equation for each precipitation reaction indicated.  $\text{AgCl(s)}$  formation is shown as an example.
- Calculate  $\Delta G^\circ$  for each reaction.
  - Waters of hydration are included in the calculation for  $\Delta G^\circ$
  - Note that for  $\text{PbCl}_2$  and  $\text{Ba(NO}_3)_2$  you will need to use  $\Delta H$  and  $\Delta S$  values to determine  $\Delta G^\circ$ . Also note that for these two compounds, you need to calculate  $\Delta G^\circ$  at 3 temperatures.
- Calculate  $\Delta G_{\text{rxn}}$  for each solid that might precipitate when equal volumes of 0.2M cation and 0.2M anion are mixed together.
- Based on your results for  $\Delta G_{\text{rxn}}$  predict whether you will observe a precipitate during the experiment.

Once you are done completing Table 1, you can begin the experiment:

1. Mix equal amounts of the provided 0.2M solutions in order to create each of the precipitation reactions you have written in Table 1. You will have to determine which solutions to use that will create the appropriate reaction.
2. Upon mixing, indicate whether there has been precipitation.
3. Based on the precipitation results, indicate whether or not your experimental results confirm or deny your theoretical/calculated results.
4. For  $\text{PbCl}_2$  and  $\text{Ba(NO}_3)_2$  mix the appropriate solutions at room temperature and record your results. (This is your T ~ 298K result.)
5. Cool the mixtures using an ice bath and record your results (This is your T ~273K result).
6. Heat the mixtures in a boiling water bath and record if any precipitation remains (This is your T ~373K result).
7. Record your observations for  $\text{PbCl}_2$  and  $\text{Ba(NO}_3)_2$  and indicate if the results confirm or deny your theoretical calculations.

**Thermodynamic Data Required for Thermo Lab Calculations**  
 $\Delta G^\circ_f$  at 298K for Solids and Ions in 1M solution

Solids	$\Delta G^\circ_f$ (kJ)	Ions (aq)	$\Delta G^\circ_f$ (kJ)
AgCl	-109.789	Cl <sup>-</sup> (aq)	-131.228
AgI	-66.19	I <sup>-</sup> (aq)	-51.57
AgNO <sub>3</sub>	-33.41	NO <sub>3</sub> <sup>-</sup> (aq)	-108.74
Ag <sub>2</sub> SO <sub>4</sub>	-618.41	SO <sub>4</sub> <sup>2-</sup> (aq)	-744.53
BaCl <sub>2</sub> ·2H <sub>2</sub> O	-1296.32	Ag <sup>+</sup> (aq)	77.01
Ba(NO <sub>3</sub> ) <sub>2</sub>	-796.59	Ba <sup>2+</sup> (aq)	-560.77
BaSO <sub>4</sub>	-1362.2	Na <sup>+</sup> (aq)	-261.905
NaCl	-384.138	Ca <sup>2+</sup> (aq)	-553.58
NaI	-286.06	Water	
NaNO <sub>3</sub>	-367.00	H <sub>2</sub> O(l)	-237.129
Na <sub>2</sub> SO <sub>4</sub> ·10H <sub>2</sub> O	-3646.85		
CaCl <sub>2</sub>	-748.1		
CaI <sub>2</sub>	-528.9		
Ca(NO <sub>3</sub> ) <sub>2</sub>	-743.07		
CaSO <sub>4</sub> ·2H <sub>2</sub> O	-1797.28		

$\Delta H^\circ_f$  and  $\Delta S^\circ_f$  for Solids and Ions in Solution

Compound (or Ion)	$\Delta H^\circ_f$ (kJ/mol)	$\Delta S^\circ_f$ (J/K·mol)
Pb <sup>2+</sup> (aq)	-2	10
Cl <sup>-</sup> (aq)	-167	56
PbCl <sub>2</sub> (s)	-359	136
Ba <sup>2+</sup> (aq)	-538	10
NO <sub>3</sub> <sup>-</sup> (aq)	-205	146
Ba(NO <sub>3</sub> ) <sub>2</sub> (s)	-992	214

**$\Delta G$  Calculations**

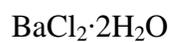
$[Ag^+] =$

$[Cl^-] =$



$[Ag^+] =$

$[SO_4^{2-}] =$



$[Ba^{2+}] =$

$[Cl^-] =$



$\Delta H^\circ_{rxn} =$

$\Delta S^\circ_{rxn} =$

$\Delta G^\circ \text{ at } 273K =$

$[Pb^{2+}] =$

$[Cl^-] =$

$\Delta G =$

**Table 1**

<b>Salt/ppt equation</b> <i>Sample equation provided for first entry only</i>		$\Delta G^{\circ}_{rxn}$ (kJ/mol)	$\Delta G_{rxn}$ (kJ/mol) <i>(hint: <math>Q \neq 1</math>)</i>	Ppt/no	Obs.
<b>AgCl</b> $Ag^{+}(aq) + Cl^{-}(aq) \rightarrow AgCl(s)$					
<b>AgI</b>					
<b>AgNO<sub>3</sub></b>					
<b>Ag<sub>2</sub>SO<sub>4</sub></b>					
<b>BaCl<sub>2</sub>·2H<sub>2</sub>O</b>					
<b>Ba(NO<sub>3</sub>)<sub>2</sub></b>					
<b>BaSO<sub>4</sub></b>					
<b>NaCl</b>					
<b>NaI</b>					
<b>NaNO<sub>3</sub></b>					
<b>Na<sub>2</sub>SO<sub>4</sub>·10H<sub>2</sub>O</b>					
<b>CaCl<sub>2</sub></b>					
<b>CaI<sub>2</sub></b>					
<b>Ca(NO<sub>3</sub>)<sub>2</sub></b>					
<b>CaSO<sub>4</sub>·2H<sub>2</sub>O</b>					
<b>PbCl<sub>2</sub></b>	<b>273K</b>				
<b>PbCl<sub>2</sub></b>	<b>298K</b>				
<b>PbCl<sub>2</sub></b>	<b>373K</b>				
<b>Ba(NO<sub>3</sub>)<sub>2</sub></b>	<b>273K</b>				
<b>Ba(NO<sub>3</sub>)<sub>2</sub></b>	<b>298K</b>				
<b>Ba(NO<sub>3</sub>)<sub>2</sub></b>	<b>373K</b>				

**Lab 6 Pre-lab Questions**

1.) Write the chemical equation corresponding to  $\Delta G^\circ_{f, 298}$  for AgCl. How does this equation differ from the net ionic equation that shows AgCl precipitating when solutions of  $\text{Ag}^+$  and  $\text{Cl}^-$  are mixed? (Write both equations and briefly explain the difference in their  $\Delta G^\circ$  calculation).

2.) The value of  $\Delta G^\circ_{f, 298}$  for  $\text{Mg}^{2+}$  is  $-454.8$  kJ/mol. The value of  $\Delta G^\circ_{f, 298}$  for  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  is  $-2114.64$  kJ/mol. Use these values as well as other thermodynamic data available on the chart supplied for this lab to perform a calculation to predict whether or not a precipitate will form when  $0.20$  M  $\text{Mg}^{2+}$  is mixed with  $0.20$  M  $\text{Cl}^-$ .