
EXPERIMENT

Thermodynamic Prediction of Precipitation Reactions



**Laboratory Time
Required**

One hour. May be combined with Experiment 29.



**Special Equipment
and Supplies**

Dropper bottles

0.2 M Solutions containing Ag^+ , Ba^{2+} , Na^+ ,
 Ca^{2+} , Pb^{2+} , Cl^- , I^- , NO_3^- , and SO_4^{2-} ions



Safety

As usual, when chemicals are used in the laboratory, safety glasses should be worn and chemicals should not be ingested.



First Aid

Wash chemicals off your skin and out of your eyes with copious amounts of water.

The chemistry curriculum has been criticized for being short on descriptive chemistry and long on theory—resulting in students who are often unfamiliar with basic phenomena and uncomfortable with chemical principles. This experiment attempts to overcome both problems by requiring you to work directly with thermodynamic concepts and calculations and to confirm your calculated predictions by direct observation of several precipitation reactions.

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PRINCIPLES

A **spontaneous change** is one that occurs by itself, without the exertion of any outside force. A mixture of hydrogen and oxygen gas changes spontaneously (and explosively) into water after being ignited by a spark. Iron rusts spontaneously, albeit slowly, when it is exposed to air and water.

Many spontaneous chemical changes, such as combustion of hydrocarbons, are exothermic. However, there are many examples of endothermic processes that occur spontaneously. These include the melting of ice at ambient temperatures above 0°C and the boiling of water at 100°C (at 760 torr of pressure). In both of these cases, spontaneous change occurs in the direction of a less-ordered state.

Two state functions have been defined to describe the tendency for a change to occur spontaneously. The first of these is ΔH , the enthalpy change. A negative value for ΔH denotes an exothermic process and is a factor that favors spontaneous change. The second state function is ΔS , the entropy change. Entropy is a measure of randomness. A positive value for ΔS denotes that the change will result in a more random (less ordered) system, a factor that also favors spontaneous change.

Very often the direction of spontaneous change is determined by temperature. For instance, water changes spontaneously into ice when placed in a freezer ($t < 0^{\circ}\text{C}$), but ice cubes melt spontaneously when removed from a freezer ($t > 0^{\circ}\text{C}$). In these cases, the signs of ΔH and ΔS work in opposition (e.g., ΔH is favorable when water freezes, but ΔS is unfavorable; ΔH is unfavorable when ice melts, but ΔS is favorable), and temperature is the factor that determines whether ΔH or ΔS will dominate. This information is incorporated into a single state function, the Gibbs free energy, ΔG , defined (for constant temperature systems) in Equation 32.1.

$$\Delta G = \Delta H - T\Delta S \quad (32.1)$$

It is easy to see that ΔG must be negative if a process is spontaneous because a change for which ΔH is negative and ΔS is positive will surely be spontaneous. Endothermic processes that give positive entropy changes will be spontaneous at high temperatures (where $T\Delta S$ dominates). Exothermic processes that give negative entropy changes will be spontaneous at low temperatures (where ΔH dominates).

Many textbooks give tabulations of values for specific free-energy changes ($\Delta G_{f,298}^{\circ}$), enthalpy changes ($\Delta H_{f,298}^{\circ}$), and entropies (S_{298}°). The $^{\circ}$ symbols indicate that the values are being given for changes involving substances in their standard states. The f subscript on ΔG and ΔH denotes formation; ΔG_f° and ΔH_f° are the free energy and enthalpy changes, respectively, which are associated with a reaction in which one mole of product is formed from its constituent elements in their standard states. The 298 subscript indicates that all quantities have been corrected to the values they would have if the change were to occur at 298K. Table 32.1 shows how to use tabulated values of $\Delta G_{f,298}^{\circ}$, $\Delta H_{f,298}^{\circ}$, and S_{298}° for carbon, oxygen, and carbon dioxide to calculate the free energy change in the combustion of carbon. Note that you can obtain the standard free energy change for any reaction, $\Delta G_{\text{rxn},298}^{\circ}$, by subtracting the sum of the $\Delta G_{f,298}^{\circ}$'s for the reactants from the sum of $\Delta G_{f,298}^{\circ}$'s for the products (see Equation 32.2).

TABLE 32.1 Calculating the Free Energy Change for the Combustion of Carbon (graphite)

	C(graphite, 298)	+ O ₂ (g, 298)	\rightleftharpoons	CO ₂ (g, 298)
$\Delta H_{f,298}^{\circ}$	0	0		-393.5 kJ/mol
S_{298}°	5.73 J/mol K	205.0 J/mol K		213.6 J/mol K
$\Delta G_{f,298}^{\circ}$	0	0		-394.3 kJ/mol
$\Delta H_{rxn,298}^{\circ} = \Delta H_{f,298}^{\circ}(\text{CO}_2) - \Delta H_{f,298}^{\circ}(\text{O}_2) - \Delta H_{f,298}^{\circ}(\text{C})$				
$\Delta H_{rxn,298}^{\circ} = -393.5 \text{ kJ/mol}$				
$\Delta S_{rxn,298}^{\circ} = S_{298}^{\circ}(\text{CO}_2) - S_{298}^{\circ}(\text{O}_2) - S_{298}^{\circ}(\text{C})$				
$\Delta S_{rxn,298}^{\circ} = 2.9 \text{ J/mol K}$				
$\Delta G_{rxn,298}^{\circ} = \Delta H_{rxn}^{\circ} - T\Delta S_{rxn}^{\circ} = -394.4 \text{ kJ/mol}$				
$\Delta G_{rxn,298}^{\circ} = \Delta G_{f,298}^{\circ}(\text{CO}_2) - \Delta G_{f,298}^{\circ}(\text{O}_2) - \Delta G_{f,298}^{\circ}(\text{C})$				
$\Delta G_{rxn,298}^{\circ} = -394.3 \text{ kJ/mol}$				

$$\Delta G_{f,298}^{\circ} = \sum_{\text{products}} \Delta G_{f,298}^{\circ} - \sum_{\text{reactants}} \Delta G_{f,298}^{\circ} \quad (32.2)$$

The combustion of carbon to give carbon dioxide is, of course, a spontaneous process. This is confirmed by the fact that G_{298}° for the combustion process is -394.4 kJ/mol . This means that when one mole of graphite, the most stable form of carbon, is combined with one mole of oxygen, at one atmosphere pressure, to produce one mole of CO_2 , at one atmosphere pressure, the free energy of the system decreases by 394.4 kJ . If the reaction is not performed with all materials in their standard states, if the reaction temperature is not 298 K , if the pressure of the either of the gases is not one atmosphere, or if more or less than one mole of carbon is consumed in the reaction, then a value of ΔG_{rxn} will be obtained that will differ from ΔG_{rxn}° . The relationship between ΔG_{rxn} and ΔG_{rxn}° is shown in Equation 32.3.

$$\Delta G_{rxn} = \Delta G_{rxn}^{\circ} + 2.303 RT \log Q \quad (32.3)$$

In Equation 32.3, R is the ideal gas constant (8.314 J/K mol), T is the Kelvin temperature, and Q denotes the reaction quotient. As is customary for evaluating equilibrium constants and reaction quotients, liquids, solids, and solvents are represented by unity; solute concentrations are represented by molarity; and the pressures of gases are given in atmospheres.

In this experiment, you will be calculating the ΔG_{rxn} for a variety of possible precipitation reactions. You will use your calculated values to predict whether a precipitate will form when two solutions are mixed. Then you will actually mix the reagents and attempt to confirm your predictions. You will also calculate ΔG_{rxn} for the precipitation of a few salts at different temperatures. You will place the precipitates in hot or cold baths and attempt to confirm your predictions regarding the change in solubility as a function of changing temperature as well. Tables 32.2 and 32.4 list the data you will use to make your calculations. The following paragraphs explain how to use this data.

The row and column headings of Table 32.2 show the standard free energies

TABLE 32.2 Gibbs Free Energies ($\Delta G_{f,298}^{\circ}$) for Ions in 1 M Solution and Solids

Anions→ ↓Cations	Cl ⁻	I ⁻	NO ₃ ⁻	SO ₄ ²⁻
	-131.228	-51.57	-108.74	-744.53
Ag ⁺ 77.107	-109.789	-66.19	-33.41	-618.41
Ba ²⁺ -560.77	-1296.32 W2	—	-796.59	-1362.2
Na ⁺ -261.905	-384.138	-286.06	-367.00	-3646.85 W10
Ca ²⁺ -553.58	-748.1	-528.9	-743.07	-1797.28 W2

of formation of the various ions under consideration, with the standard state as a 1 M solution. Thus, $\Delta G_{f,298}^{\circ}$ for Ag⁺ is 77.107 kJ/mol and $\Delta G_{f,298}^{\circ}$ for Cl⁻ is -131.228 kJ/mol. Entries within the body of the table show the standard free energies of formation for the crystalline solids that result from the combinations of the various ions whose rows and columns intersect to create the compound's cell. For instance, $\Delta G_{f,298}^{\circ}$ for AgCl is -109.789 kJ/mol. The "W10" entry in the cell corresponding to sodium sulfate indicates that the most likely precipitate is Na₂SO₄·10H₂O. When you write the equation for the precipitation of such a hydrated salt, water will appear as a reactant. Therefore, in the calculation of $\Delta G_{\text{rxn}}^{\circ}$ you will need to consider $\Delta G_{f,298}^{\circ}$ for water, which has a value of -237.129 kJ/mol.

Because you will not be working with 1 M solutions, the free-energy changes you will be calculating will not be standard free energies; rather, Equation 32.3 will be needed to convert the ΔG° 's to ΔG 's. Table 32.3 shows the calculation of ΔG for the possible reaction between Ag⁺ ions and Cl⁻ ions to form the precipitate, silver chloride. Because $\Delta G_{\text{rxn},298}^{\circ}$ for the precipitation of AgCl is negative, it is predicted that the precipitate will form when solutions of Ag⁺ and Cl⁻ ions are mixed.

TABLE 32.3 Calculating ΔG for the Precipitation of AgCl

$$\text{Ag}^+ (0.1 \text{ M}) + \text{Cl}^- (0.1 \text{ M}) \longrightarrow \text{AgCl} (\text{s})$$

$$\Delta G_{\text{rxn},298}^{\circ} = \Delta G_{f,298}^{\circ} (\text{AgCl}) - \Delta G_{f,298}^{\circ} (\text{Ag}^+) - \Delta G_{f,298}^{\circ} (\text{Cl}^-)$$

$$\Delta G_{\text{rxn},298}^{\circ} = -109.789 - (77.107) - (-131.228) \text{ kJ/mol}$$

$$\Delta G_{\text{rxn},298}^{\circ} = -55.668 \text{ kJ/mol}$$

$$\Delta G_{\text{rxn},298} = \Delta G_{\text{rxn},298}^{\circ} + 2.303 RT \log Q$$

$$\Delta G_{\text{rxn},298} = -55.668 \text{ kJ/mol} + 2.303 \frac{(8.314 \text{ J/mol K})(298 \text{ K})}{1000 \text{ J/kJ}} \log \frac{1}{(0.1)(0.1)}$$

$$\Delta G_{\text{rxn},298} = -44.250 \text{ kJ/mol}$$

The ΔG° 's and ΔG 's you have calculated so far were evaluated at 298K. There will be times when you may wish to evaluate these functions at other temperatures. This is easily accomplished because the values of ΔH° and ΔS° are relatively independent of temperature. Thus, ΔG° can be evaluated at any temperature by the use of Equation 32.4, where T is the Kelvin temperature and ΔH_{298}° and ΔS_{298}° are the enthalpy and entropy change, respectively, for the reaction.

$$\Delta G_T^\circ = \Delta H_{298}^\circ - T \Delta S_{298}^\circ \quad (32.4)$$

Values of $\Delta H_{f,298}^\circ$ and S_{298}° for several ions and crystalline solids are given in Table 32.4. Use the values given to decide whether precipitates would form when equal volumes of 0.2 M solutions of Pb^{2+} and Cl^- are mixed at 273K, 298K, and 373K. Do similar calculations for mixtures of equal volumes of 0.2 M solutions of Ba^{2+} and NO_3^- . Use Equation 32.4 to evaluate ΔG_T° at $T = 273\text{K}$, 298K, and 373K. Use Equation 32.3 to evaluate ΔG_T at those temperatures. An example of this kind of calculation is given in Table 32.5. Because $\Delta G_{\text{rxn},273}$ is negative for the precipitation reaction, it is predicted that a precipitate will form if equal volumes of 0.2 M Pb^{2+} and 0.2 M I^- are mixed and cooled to 273K.

TABLE 32.4 Values of $\Delta H_{f,298}^\circ$ and S_{298}° for Various Ions and Solids

	$\Delta H_{f,298}^\circ$ kJ/mol	S_{298}° J/K mol
Pb^{2+}	- 2	10
Cl^-	-167	56
PbCl_2	-359	136
I^-	- 55	111
PbI_2	-175	175
Ba^{2+}	-538	10
NO_3^-	-205	146
$\text{Ba}(\text{NO}_3)_2$	-992	214

TABLE 32.5 Calculating ΔG for the Precipitation of PbI_2 at 273 K

$\text{Pb}^{2+} (0.1 \text{ M}) + 2 \text{I}^- (0.1 \text{ M}) \longrightarrow \text{PbI}_2 (\text{s})$
$\Delta H_{\text{rxn},298}^\circ = -175 - (-2 + 2(-55)) = -63 \text{ kJ}$
$\Delta S_{\text{rxn},298}^\circ = 175 - (10 + 2(111)) = -57 \text{ J/K}$
$\Delta G_{\text{rxn},273}^\circ = -63000 - 273(-57) = -46 \times 10^3 \text{ J}$
$\Delta G_{\text{rxn},273} = -46 \times 10^3 \text{ J} + (2.303)(8.314)(273) \log (1/(0.1)(0.1))$
$\Delta G_{\text{rxn},273} = -46 \times 10^3 \text{ J} + 10.5 \times 10^3 \text{ J} = -36 \times 10^3 \text{ J}$

PROCEDURE

Calculate the value of $\Delta G_{\text{rxn},298}$ for each solid that might result when each of the 0.2 M solutions of cations listed in Table 32.2 is mixed with an equal volume of each of the anion solutions listed. Note that mixing equal volumes of 0.2 M solutions of cations and anions will result in 0.1 M solutions after mixing. Record your values of the ΔG 's in the upper space of the boxes on the Summary Report sheet. Then mix the solutions and note in the lower spaces whether your observations confirm (C) or deny (D) your predictions. Below the table of results, note the appearance of the precipitates you observe and briefly discuss possible reasons for any discrepancies between your predictions and your observations.

Also, calculate the values of $\Delta G_{\text{rxn}, T}$ for the precipitation of PbCl_2 and $\text{Ba}(\text{NO}_3)_2$ from solutions that are 0.1 M in lead ions and chloride ions and 0.1 M in barium ions and nitrate ions, respectively, for $T = 273\text{K}$, 298K , and 373K . Mix the appropriate solutions at room temperature. If no precipitate results, cool the mixture in an ice bath. If a precipitate does appear, heat the test tube containing the precipitate and supernatant liquid in a boiling water bath.

Note whether the precipitate dissolves and whether your observations are in accord with your calculations. If they are not, briefly discuss possible reasons for the discrepancies.

Disposal of Reagents

The small quantities of chemicals used in this experiment may be flushed down the drain with copious amounts of water.

