

EXPERIMENT B8: EFFECT OF TEMPERATURE ON EQUILIBRIUM CONSTANT

Learning Outcomes

Upon completion of this lab, the student will be able to:

- 1) Predict the effect of temperature on the equilibrium constant.
- 2) Design an experiment to measure the thermodynamic parameters for the dissolving of metal hydroxides in water.

Introduction

When ionic compounds are dissolved in water, it is generally assumed that increasing the temperature will cause more of the solid to dissolve. However, this assumption is not always true, as will be demonstrated in this experiment.

In this experiment, calcium hydroxide will be dissolved in water and the effect of temperature on this process will be studied. The data from the experiment will not only be used to determine the effect of temperature on the equilibrium constant, but also to determine thermodynamic parameters such as ΔH , ΔS , and ΔG for the process.

Several concepts discussed throughout this class will be examined in this experiment. These include:

- a. Effect of temperature on equilibrium
- b. Relationship between pH and equilibrium constant for a saturated solution
- c. Determination of thermodynamic parameters such as ΔH and ΔS .

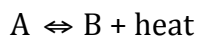
Effect of temperature on equilibrium

According to Le Chatelier's principle, "when a system at equilibrium is subjected to change in concentration, temperature, volume, or pressure, then the system readjusts itself to (partially) counteract the effect of the applied change and a new equilibrium is established".

In this section, the effect of temperature on the equilibrium process will be further examined.

The effect of temperature on the equilibrium process depends on whether the reaction is exothermic or endothermic. Exothermic reactions are those in which the system generates heat and as a result heat may be considered as a product (an output) of these reactions. On the other hand, endothermic reactions are those in which the system absorbs heat and as a result heat may be considered as a reactant (an input) of these reactions.

Consider the exothermic transformation of A to B. Since heat is generated in this reaction, the equation can be written as:



If heat is added to this reaction, i.e., if the temperature is increased, the equilibrium will shift left and produce more A. Conversely, if heat is removed from this reaction, i.e., if the temperature is decreased, the equilibrium will shift right and produce more B.

Therefore, in general, increasing the temperature of an exothermic reaction shifts the equilibrium in the direction of the reactants and vice versa.

Now, consider the endothermic transformation of C to D. Since heat is absorbed in this reaction, the equation can be written as:

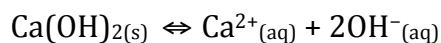


If heat is added to this reaction, i.e., if the temperature is increased, the equilibrium will shift right and produce more D. Conversely, if heat is removed from this reaction, i.e., if the temperature is decreased, the equilibrium will shift left and produce more C.

Therefore, in general, increasing the temperature of an endothermic reaction shifts the equilibrium in the direction of the products and vice versa.

Relationship between pH and equilibrium constant for a saturated solution

A saturated solution is obtained when the maximum amount of solute has been dissolved in a given amount of solvent. In a saturated solution of an ionic substance in water, the solute is in equilibrium with the aqueous ions. For instance, in a saturated solution of calcium hydroxide:



The equilibrium constant for this process is given by:

$$K = [\text{Ca}^{2+}][\text{OH}^{-}]^2$$

Note the absence of $\text{Ca(OH)}_{2(s)}$ in the expression for the equilibrium constant. Since the amount of a solid is generally thought to be unchanged, it is excluded from the equilibrium constant expression.

The following equilibrium table shows how the equilibrium constant is calculated for such a process. In the table, "I" is assumed to be some initial amount of the solid

calcium hydroxide, and “x” is the amount of the solid that dissolves in water to form the aqueous ions.

	$\text{Ca(OH)}_{2(s)}$	\rightleftharpoons	$\text{Ca}^{2+}_{(aq)}$	+	$2\text{OH}^{-}_{(aq)}$
Initial concentrations	I		0		~0
Amount that dissolves	-x		+x		+2x
Equilibrium amount	I - x		x		2x

Therefore:

$$K = [\text{Ca}^{2+}][\text{OH}^{-}]^2$$

$$K = x \times (2x)^2 = 4x^3$$

In order to determine the equilibrium constant K, “x” must be known.

How can “x” be determined experimentally?

In a previous experiment (Experiment B4), “x” was determined spectrophotometrically. In that case, the product was colored and such a determination was therefore possible.

In this situation however, spectrophotometric determination is not a simple option.

A close examination of the equilibrium table above shows that:

$$2x = [\text{OH}^{-}]$$

$$\text{Therefore: } x = \frac{[\text{OH}^{-}]}{2}$$

The concentration of hydroxide, $[\text{OH}^{-}]$, is related to the hydrogen ion concentration, $[\text{H}^{+}]$, and therefore to the pH of the solution, by the ionic product of water.

$$K_w = 1.0 \times 10^{-14} = [\text{H}^{+}] \times [\text{OH}^{-}]$$

$$\text{pH} = -\log[\text{H}^{+}]$$

In summary, if the pH of the saturated solution is determined, the $[\text{H}^{+}]$ can be ascertained. Using the ionic product of water, one can then determine the $[\text{OH}^{-}]$. Knowing the $[\text{OH}^{-}]$ one can calculate “x” and therefore K.

Determination of thermodynamic parameters such as ΔH , ΔS , and ΔG

As discussed earlier, chemical equilibrium is impacted by changes in temperature. The relationship between the absolute temperature, T, and the equilibrium constant, K, for a reaction is given in Equation 1 below:

$$\Delta G^\circ = -RT \ln K \quad \text{Equation 1}$$

In Equation 1, ΔG° is the standard free energy change and R is the universal gas constant (8.314 J/mol-K).

By definition, the standard free energy change, ΔG° is also related to the standard enthalpy change, ΔH° and the standard entropy change, ΔS° according to Equation 2.

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad \text{Equation 2}$$

In thermodynamics, the values of ΔH° and ΔS° may generally be considered to be invariable when the temperature is changed and the value of ΔG° on the other hand changes with temperature.

Therefore, Equations 1 and 2 may be combined as follows:

$$-RT \ln K = \Delta H^\circ - T\Delta S^\circ \quad \text{Equation 3}$$

Equation 3 can further be manipulated to isolate the dependent variables and the constants. Dividing both sides of the equation by “-RT” results in Equation 4.

$$\ln K = -\frac{\Delta H^\circ}{R} \left(\frac{1}{T} \right) + \frac{\Delta S^\circ}{R} \quad \text{Equation 4}$$

In Equation 4, ΔH° , ΔS° , and R are constants and K and T are variables.

A comparison of Equation 4 with the equation of a straight line, $y = mx + b$, indicates the following:

$$\begin{aligned} \ln K &\text{ is analogous to } y \\ \frac{1}{T} &\text{ is analogous to } x \\ -\frac{\Delta H^\circ}{R} &\text{ is analogous to } m \\ \frac{\Delta S^\circ}{R} &\text{ is analogous to } b \end{aligned}$$

Therefore a linear regression of a plot of $\ln K$ vs. $\frac{1}{T}$ should result in a straight line whose slope will be $-\frac{\Delta H^\circ}{R}$ and whose y-intercept will be $\frac{\Delta S^\circ}{R}$. Since R is the universal gas constant, the values of ΔH° and ΔS° can be determined from the slope and the intercept, respectively of the best fit line.

Experimental Design

A saturated solution of calcium hydroxide will be provided for this experiment. This solution will be heated to about 70°C and the pH of the solution will be determined using a pH meter. The solution should then be cooled in about 5°C intervals down to about 5°C and the pH determined at each intermediate temperature. The pH of the solution will be used to determine the $[H^+]$ at each temperature. This will then be converted to $[OH^-]$ and then K at each temperature. A plot of $\ln K$ vs. $1/T$ will be used to determine the various thermodynamic parameters.

Reagents and Supplies

Saturated solution of $Ca(OH)_2$, pH meter, hot plate, thermometer

(See posted Material Safety Data Sheets)

Procedure

1. Read the complete instruction manual for the operation of a pH meter.
2. Obtain a pH meter, thermometer, and a hot plate from the stockroom.
3. The instructor will demonstrate the proper use and calibration of the pH meter. The instructor will also demonstrate how to adjust the temperature setting of the pH meter. This setting must be adjusted for each temperature at which the pH will be measured.
4. Set up a hot water bath. In order to do this, half fill a large beaker with tap water and place on a hot plate. Heat the water to about 70-75°C. Monitor the temperature with a thermometer.
5. Obtain about 10 mL of saturated Ca(OH)_2 solution in a large test tube. Add a small amount of solid Ca(OH)_2 to the test tube to ensure that the solution is indeed saturated.
6. Obtain a ring stand and a clamp and suspend the test tube containing the Ca(OH)_2 into the water bath ensuring that the solution is completely submerged inside the water.
7. Measure and record the temperature of the Ca(OH)_2 solution. Aim to start measurements at around 70°C.
8. Measure and record the pH of the Ca(OH)_2 solution.
9. Cool the water bath by about 5°C using room temperature water at first and then cold water or ice. Repeat steps 7 and 8 and obtain measurements in about 5°C intervals until the temperature has reached 5°C.
10. Discard the Ca(OH)_2 solution in an appropriate waste container provided by the instructor.

Data Analysis

1. Calculate the $[H^+]$ from the pH measured at each temperature.

$$[H^+] = 10^{-pH}$$

2. Calculate the $[OH^-]$

$$[OH^-] = \frac{1.0 \times 10^{-14}}{[H^+]}$$

3. Calculate "x".

$$x = \frac{[OH^-]}{2}$$

4. Calculate K.

$$K = 4x^3$$

5. Calculate $\ln K$ (natural logarithm of K)

6. Convert all temperatures to the Kelvin scale and calculate $\frac{1}{T}$

7. Plot a graph of $\ln K$ (y-axis) vs. $\frac{1}{T}$ (x-axis).

8. Use regression analyses to find the equation of the best fit linear equation for the data and obtain the slope (m) and the y-intercept (b).

9. Using the slope, calculate the value of ΔH° .

$$\text{slope}(m) = -\frac{\Delta H^\circ}{R}$$

$$\Delta H^\circ = -(\text{slope} \times R)$$

10. Using the y-intercept, calculate the value of ΔS° .

$$y - \text{intercept} = \frac{\Delta S^\circ}{R}$$

$$\Delta S^\circ = R \times (y - \text{intercept})$$

NOTE: Steps 1 through 7 of the data analysis may be completed using a spreadsheet program such as Microsoft Excel.

	A	B	C	D	E	F	G	H	I
1	Temperature, T °C	pH	[H ⁺]	[OH ⁻]	x	K	T, Kelvin	1/T	ln(K)
2	70	pH ₁	=10 ^{^(-B2)}	=(1.0E-14)/C2	=D2/2	=4*((E2)^3)	=A2+273.15	=1/G2	=LN(F2)
3	65	pH ₂							
4	60	pH ₃							
5	55	pH ₄							
6	50	pH ₅							
7	45	pH ₆							
8	40	pH ₇							
9	35	pH ₈							
10	30	pH ₉							
11	25	pH ₁₀							
12	20	pH ₁₁							
13	15	pH ₁₂							
14	10	pH ₁₃							
15	5	pH ₁₄							

1. Enter the data (temperature in °C and pH) in columns A and B. Use Row 1 for column headings.
2. Enter formulas in Row 2 for each calculation, as shown in the table above.
3. In each column, point the cursor to the bottom right corner of a cell (say C2) and drag down (till Row 15) the plus sign to copy the formula to the other cells. Repeat this for all the columns D through I.
4. To draw a graph, select the x and y data, which would be data in fields H:2-15 and I:2-15.
5. Click "Insert" and then "Chart". Choose "XY" scatter and select "Marked Scatter"
6. When the graph is displayed, click on any data point on the chart and from the toolbar, select "Chart" and then "Insert Trendline".
7. From the pop-up box, select the "Options" tab and check the boxes: 1) Display equation and 2) Display R-squared value and click OK.

Results

1. What happens to the equilibrium constant for the process of dissolving $\text{Ca(OH)}_{2(s)}$ in water, when the temperature is increased?
2. Based on the observation reported in question 1, comment on the effect of temperature on the solubility of calcium hydroxide.
3. The experimental values of the thermodynamic parameters for the dissolving of $\text{Ca(OH)}_{2(s)}$ in water are:

$$\Delta H^\circ = \text{_____ kJ/mol}$$

$$\Delta S^\circ = \text{_____ J/mol-K}$$

4. Are the results consistent with the observations?

5. Use thermodynamic tables to determine the theoretical values of the thermodynamic parameters. The theoretical values of the thermodynamic parameters for dissolving of $\text{Ca(OH)}_{2(s)}$ in water are (show each calculation):

$$\Delta H^\circ = \text{_____ kJ/mol}$$

$$\Delta S^\circ = \text{_____ J/mol-K}$$

6. The percentage error in the experimental results are:

$$\Delta H^\circ = \text{_____}$$

$$\Delta S^\circ = \text{_____}$$

7. What are the sources of error in this experiment?