18. Spontaneity

Introduction

What is the criterion or requirement for the spontaneity of a physical or chemical process? Students often believe that every exothermic process must be spontaneous. However, the sole criterion at constant temperature and pressure (Ebbing/Gammon, Section 18.4) is

$$\Delta H - T\Delta S < 0$$

As you know, ΔH and ΔS are the enthalpy and entropy changes for the process. The entire left-hand side of this inequality is called the *free-energy change*. The symbol for this change is ΔG. There are three rules that are easy to remember. If ΔG is negative ($\Delta G < 0$), the process is spontaneous. If it is positive ($\Delta G > 0$), the process is nonspontaneous. If it is zero, the process is at equilibrium.

Purpose

Using thermochemical methods, you will measure the enthalpy change that occurs when sodium nitrate is dissolved in water. You will also predict the sign of the free-energy change for this process and estimate the minimum value for the entropy change.

Concept of the Experiment

The process that you will examine in this experiment is given by the equation

$$NaNO_3(s) \rightleftharpoons Na^+(aq) + NO_3^-(aq)$$

You will measure the heat evolved or absorbed during this process by using the coffee-cup calorimeter. Appendix B describes this calorimeterand gives definitions of the system and its surroundings in terms of this calorimeter. If you did the experiment "Thermochemistry and Hess's Law" or "A Student's View of Liquids and Solids," you will be familiar with the calorimeter, the technique, and the calculations that give you the enthalpy change for the process. You will pool your data with those of your classmates to obtain better precision in the measured enthalpy change.

After you have obtained ΔH, you will have to decide whether the process is spontaneous or nonspontaneous. The sign of ΔG for the process will rest on your decision. Finally, you should be able to obtain a minimum value for the entropy change (as well as its sign) from ΔH and the predicted sign for ΔG.

Procedure

Getting Started

1. Work with a partner.
2. Obtain a coffee-cup calorimeter.

Measuring the Heat Evolved or Absorbed

1. In the Prelaboratory Assignment, you calculated the mass of $NaNO_3$ that would be required to prepare 100 mL of a 1.0 *M* solution. Using the laboratory balance, weight out this mass of $NaNO_3$. Make sure the pan of the balance is protected by placing the sodium nitrate onto a piece of weighing paper.

2. Place 100 mL of distilled water in the calorimeter, using a clean 100-mL graduated cylinder.
3. Measure and record the temperature of this water to the nearest 0.1°C. This is the initial temperature (t_i).
4. Add the solid $NaNO_3$ to the cup in such a way that none adheres to the side of the cup.
5. Place the top on the calorimeter immediately and begin stirring.
6. Measure the temperature of the solution to the nearest 0.1°C after 30 s and every 30 s thereafter until the temperature attains either a maximum or a minimum value. This temperature will be used as the final temperature (t_f).
7. Calculate q(system), using 4.184 J/(g • °C) and 1.0 g/mL for the specific heat and density of the solution and 1.0×10^1 J/°C for the heat capacity of the calorimeter. (Refer to Appendix B for details on how to do these calculations.)
8. Calculate the enthalpy change, ΔH, from q(system) and the number of moles of $NaNO_3$.
9. Repeat Steps 1 through 8 with a new solution. Calculate the mean enthalpy change for the process.
10. Pool this value with the data obtained by your classmates, and calculate a new mean enthalpy change.

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Prelaboratory Assignment

1. Provide symbols (where appropriate) and definitions for the following terms:

   a. Enthalpy change

   b. Entropy change

   c. Free-energy change

   d. Spontaneous process

   e. Nonspontaneous process

2. a. How will you decide whether a process is spontaneous in this experiment?

b. If you were to use this method after you had observed the fate of an ice cube at 25°C, what would you conclude about the spontaneity of the following process? Why?

$$H_2O(s) \rightleftarrows H_2O(l)$$

\c. The standard enthalpy change for this process is 6.01 kJ/mol. What is the minimum value for the standard entropy change, based on your conclusions about the spontaneity of this process?

3. During this experiment, you will be required to prepare 100 mL of a 1.0 *M* solution of $NaNO_3$. Calculate the mass of $NaNO_3$ (to the nearest tenth of a gram) that will be required.

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Results

Trial	1	2
Mass of $NaNO_3$ and paper (g)		
Mass of paper (g)		
Mass of $NaNO_3$ (g)		
t_i (°C)		
Temperature (°C) after		
30 s		
60 s		
90 s		
120 s		
150 s		
180 s		
210 s		
240 s		
t_f(°C		
q(system) (J)		
ΔH (kJ/mol)		
Mean ΔH (kJ/mol)		

Calculations:

Pooled results (Include your own mean ΔH.)

______ ______ ______ ______ ______

______ ______ ______ ______ ______

______

Mean ΔH: ______

Questions

1. Is the process

$$NaNO_3(s) \rightleftharpoons Na^+(aq) + NO_3^-(aq)$$

spontaneous or nonspontaneous? Why?

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2. a. Use your experimental data and your decision about the spontaneity to calculate a minimum value for the entropy change for the process.

   b. Does the sign of the entropy change predicted by this method agree with the one that you would predict on the basis of the expected change in disorder as solid $NaNO_3$ is dissolved in water? Explain.

3. Many students believe that spontaneous processes must be exothermic. Does your data from this experiment support this theory? Why or why not?