

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

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

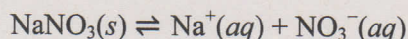
As you know, ΔH and ΔS are the enthalpy and entropy changes for the process. The entire left-hand side of this inequality is called the *free-energy change*. The symbol for this change is ΔG . There are three rules that are easy to remember. If ΔG is negative ($\Delta G < 0$), the process is spontaneous.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



You will measure the heat evolved or absorbed during this process by using the coffee-cup calorimeter. Appendix B describes this calorimeter and 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 $q(\text{system})$, using $4.184 \text{ J}/(\text{g} \cdot ^\circ\text{C})$ and 1.0 g/mL for the specific heat and density of the solution and $1.0 \times 10^1 \text{ J}/^\circ\text{C}$ 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 $q(\text{system})$ 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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Course/Section _____
Instructor _____

Student Name _____
Team Members _____

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Prelaboratory Assignment

Trial _____ 1 _____ 2 _____

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

a. Enthalpy change

b. Entropy change

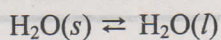
c. Free-energy change

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?



- 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 NaNO₃. Calculate the mass of NaNO₃ (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)	_____	_____
$q(\text{system})$ (J)	_____	_____
ΔH (kJ/mol)	_____	_____
Mean ΔH (kJ/mol)	_____	

Calculations:



Results

Trial _____

Mass of $NaNO_3$ and paper (g) _____

Mass of paper (g) _____
The standard enthalpy change for this process is 6.0 kJ/mol. What is the minimum amount of $NaNO_3$ required to heat the water to boiling? What is the minimum amount of $NaNO_3$ required to heat the water to boiling? What is the minimum amount of $NaNO_3$ required to heat the water to boiling?

Mass of $NaNO_3$ (g) _____

ΔT (°C) _____

Temperature (°C) after _____

30 s _____

60 s _____

90 s _____

120 s _____

150 s _____

180 s _____

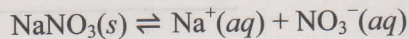
210 s _____

240 s _____

Mean ΔH (kJ/mol) _____

Questions

1. Is the process



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.

Introduction

We encounter oxidation-reduction reactions every day. Examples include the combustion of coal, natural gas, oil, and gasoline, the operation of an automobile's battery, and the removal of stains by a bleach.

Although there are a variety of oxidation-reduction reactions, when you compare a number of these reactions, you can find some common features. Each reaction consists of simultaneous oxidation and reduction because electrons are lost by one atom and gained by another one. Moreover, the reactants must include an oxidizing agent and a reducing agent. Electrons are always lost by the reducing agent and gained by the oxidizing agent (Libbing/Garrison, Section 4.5).

Purpose

You will observe the reactions of the halogens and their halides. On the basis of these observations, you will be able to rank the halogens according to their oxidizing strengths and the halides according to their reducing strengths. Your subsequent observations on the reactions of two common oxidizing agents will enable you to rank the latter according to their oxidizing strengths. You will also find that the products obtained from an oxidation-reduction reaction in an acidic solution can differ markedly from those obtained in a basic solution. Finally, and most important, you will write a balanced equation for each reaction that you have observed.

The Halogens and the Halides

You will deal with halogens and halides in each part of this experiment. A brief description of some of

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

The halogens are found in Group VIIA of the periodic table. The members of this group are fluorine (F₂), chlorine (Cl₂), bromine (Br₂), iodine (I₂), and astatine (At₂). Because these elements belong to the same group, they have many similar properties. For example, their elemental form is diatomic (F₂, Cl₂, Br₂, I₂, and At₂), and each of them is an oxidizing agent. This experiment uses only Cl₂, Br₂, and I₂, however, because F₂ is such a strong oxidizing agent that special conditions are required for its study and because astatine is radioactive.

Aqueous solutions of Cl₂, Br₂, and I₂ can be prepared either by dissolving these elements in water or by generating them in solution as products of certain oxidation-reduction reactions. Aqueous solutions of these halogens are called chlorine water, bromine water, and iodine water, respectively. Each solution has its own characteristic color, depending on the concentration and the pH of the solution. Chlorine water is colorless to yellow; bromine water is yellow to red-brown; and iodine water is red-brown to brown.

These halogens are also soluble in cyclohexane (C₆H₁₂), a substance that is itself insoluble in water. When cyclohexane is added to an aqueous solution of a halogen, two layers are formed. The upper layer is cyclohexane, because it is insoluble and less dense than water. A portion of the halogen passes from the aqueous layer to the upper cyclohexane layer (a process called *extraction*). A characteristic color is then imparted to this layer. The color of a halogen in cyclohexane differs somewhat from its color in an aqueous solution, as you will discover during the experiment.