4.1.7 ENTROPY-DRIVEN REACTIONS

Concepts to Investigate: Gibbs free energy, spontaneity, entropy, enthalpy, second law of thermodynamics.

Materials: Ammonium thiocyanate (NH_4SCN), barium hydroxide octahydrate ($Ba(OH)_2 \cdot 8H_2O$), mortar and pestle, small block of wood.

Safety: *Because of cost and safety issues this activity should be performed only as a teacher demonstration. Wear goggles, lab coat and gloves.*

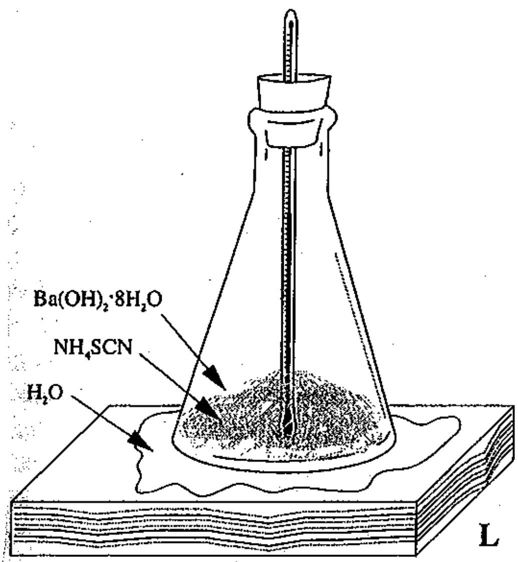
Principles and Procedures: Although it is not surprising to see a cone fall from a pine tree, it would be startling to see it rise spontaneously from the ground. Scientists have long recognized the tendency of processes to occur that lead to lower (more stable) energy states. The potential energy of a pine cone on the ground is less than in the tree, so cones can fall spontaneously, but cannot rise spontaneously. Such observations led many 19th-century scientists to believe that spontaneous reactions are always exothermic and result in a decrease in heat energy (enthalpy, H). If this were true, then all spontaneous reactions would be exothermic, but, as we shall see in this activity, this is not the case. There are many reactions that are endothermic, and yet occur spontaneously.

We now know that two factors influence the drive to spontaneous change—the tendency toward lowest heat energy (enthalpy, H), and the tendency toward greatest disorder (entropy, S). The enthalpy/entropy function of a system is the energy available to do useful work (Gibbs free energy, G). At constant temperature and pressure, the free-energy change (the chemical reaction potential, ΔG) of a system can be expressed as the difference between the change in enthalpy (ΔH), and the product of the Kelvin temperature and the entropy change ($T\Delta S$):

$$\Delta G = \Delta H - T\Delta S$$

Whenever the change in free energy is negative (free energy is lost from the system) the reaction is spontaneous. Losses in heat energy (negative ΔH as in exothermic reactions) and increases in randomness (positive ΔS) increase the driving force of the reaction (move ΔG in the negative direction), while gains in heat energy (a positive ΔH, as in endothermic reactions) and decreases in randomness (negative ΔS) reduce the driving force of the reaction (move ΔG in the positive direction). Thus, while the majority of spontaneous reactions (reactions with a negative ΔG) are exothermic (negative ΔH), endothermic reactions (positive ΔH) may be spontaneous if the increases in temperature/entropy term *($T\Delta S$)* outweigh the gain in enthalpy. In this activity we shall investigate such a reaction.

Carefully grind approximately 20 grams of barium hydroxide octahydrate ($Ba(OH)_2 \cdot 8H_2O$) to a fine powder with a mortar and pestle. Mix the powdered barium hydroxide with approximately 10 grams of ammonium thiocyanate (NH_4SCN) in a 250 mL Erlenmeyer flask. Seal the flask with a stopper fitted with a thermometer as shown in Figure L. Swirl the flask and record the temperature at five second intervals. As a liquid starts to appear in the flask, set the flask on a small block of wood whose surface has been thoroughly wetted. As the reaction proceeds, heat will be removed from the water on the board, causing the water to freeze and the flask to stick to the board. Carefully lift the flask (Figure M).



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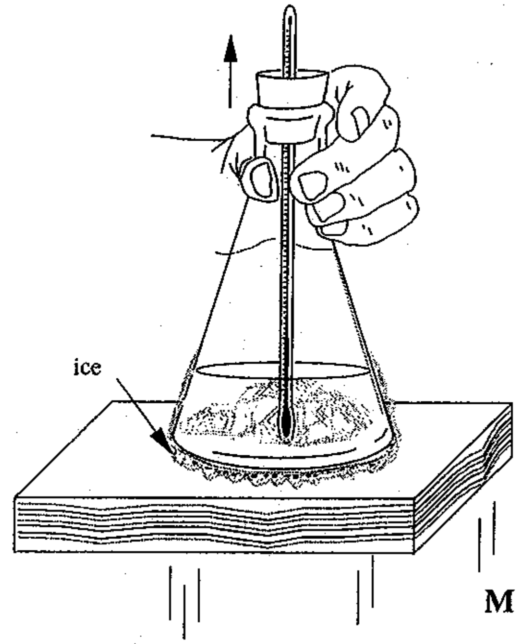


M

Does the block come with it? What is the coldest temperature reached by the liquid in the flask? The following equation describes the reaction:

$$Ba(OH)_2 \cdot 8H_2O(s) + 2NH_4SCN(s) \longrightarrow Ba^{2+}(aq) + 2SCN^{-1}(aq) + 2NH_3(aq) + 10H_2O(l)$$

Open the flask and carefully waft the fumes toward you, keeping your face at least a half a meter from the flask. Never sniff any chemical! Can you detect an ammonia odor?

Questions

(1) Of the three states of matter (solid, liquid, gas), which has the highest entropy (most random state)? Explain.

(2) For this highly endothermic reaction to proceed spontaneously, there must be a significant increase in entropy. Examine the reaction and explain the reason for this increased entropy.

(3) How cold did the liquid in the flask get?

(4) This combination of chemicals is never used in medical cold packs. Explain.

4.1.8 ENTROPY AND ENTHALPY

Concepts to Investigate: Entropy, enthalpy, free energy, Gibbs free energy equation, spontaneous processes.

Materials: Wide rubber bands, goggles, ring stand, paper clips, weights, hair dryer.

Safety: *Wear goggles.*

Principles and Procedures:

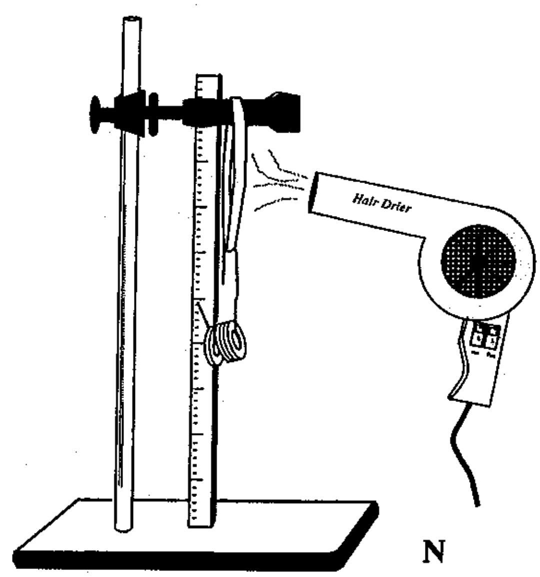
Part 1: *Put on goggles!* Hold a strong, wide rubber band tightly across your forehead. Quickly stretch the rubber band while keeping it pressed to your skin. Does the temperature of the rubber band increase or decrease? After approximately 20 seconds, relax the rubber band. Does the temperature rise or fall when the rubber band is relaxed?

The stretching of the band is not a spontaneous process because it will not occur without energy from the outside. We know that stretching the band is exothermic (negative ΔH) since heat is released and felt by thermoreceptors in the skin. An analysis of the Gibbs free energy equation indicates that if ΔG is positive, and ΔH is negative, then the change in entropy (ΔS) must be negative if the equation is to be balanced:

$$\Delta G = \Delta H - T\Delta S$$

Thus, the arrangement of molecules in a stretched rubber band must be less random (lower entropy) than when relaxed.

Part 2: Place a wide rubber band over a lateral post on a ringstand. Using a paper clip, hang weights (fishing weights, washers, balance weights, etc.) from the rubber band until it is fully stretched as shown in Figure N. Measure the length of the rubber band, and then heat it with a hair drier. Does the rubber band shorten or lengthen? Is this what you expected? Record the percentage change in length.



N

Questions

(1) Is the relaxation of the rubber band a spontaneous process? Explain. Is the ΔG value of the rubber band relaxation process positive or negative? Explain.

(2) Is stretching the band exothermic or endothermic? Is the contraction of the band exothermic or endothermic? Explain.

(3) Did the rubber band shrink or expand when heated?

(4) Is the arrangement of molecules more orderly when stretched or relaxed? Is the entropy of the band greater when stretched or relaxed? Explain.

(5) What is the driving force that causes a stretched band to contract (relax)?

(6) Why does heating the stretched rubber band cause it to contract?