Rubber Bands, Free Energy, and Le Châtelier's Principle

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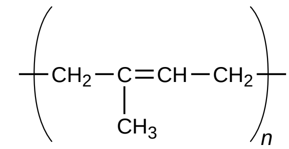
This Activity uses rubber bands to illustrate multiple concepts, including Gibbs free energy, entropy, and enthalpy. The temperature change of a rubber band that is quickly stretched is compared to one that is quickly relaxed. The effect of heating a rubber strip is also investigated.

Background



Natural rubber is a polymer of isoprene with long chains of the structure shown. Synthetic rubbers are linear polymers with similar structures. The elasticity of rubber is a consequence of the different degrees of order of these chains in the stretched and unstretched states (*1*, *2*). Models of the two states are shown on the Student Side. The stretched configuration is more ordered—of lower entropy. When released, it will revert to the more disordered, higher entropy, unstretched state. Therefore, ΔS, the entropy change, is negative for stretching. In the stretched state, the molecules are better aligned and there are stronger intermolecular attractions. Since formation of such attractions is exothermic, there is heat transfer to the surroundings when rubber is stretched. That is, stretching has a negative enthalpy change, ΔH. For a process to occur spontaneously at constant temperature and pressure, ΔG (= $\Delta H - T\Delta S$), the change in Gibbs free energy, must be negative. Since T is always positive, a negative enthalpy change and a positive entropy change favor spontaneity. However, both factors need not be favorable for spontaneity; one is sufficient provided the temperature is appropriate.

Le Châtelier's principle concerning the effect of stresses on equilibria is also a useful tool in predicting changes. Once it is established that stretching a rubber strip is exothermic, the fact that heating a stretched rubber band causes it to shrink may be explained.

Integrating the Activity into Your Curriculum

There is considerable literature about using rubber bands to teach the concepts of endothermic and exothermic processes, spontaneous and non-spontaneous processes, Le Châtelier's principle, structure-related entropy in polymers, and Gibbs free energy (*3–6*). This Activity deals with all of the preceding ideas, as well as the interplay of enthalpy and intermolecular forces. It is suitable for an advanced high school or college-level general chemistry course.

About the Activity

A rubber band that is stretched and quickly touched to the forehead feels noticeably warm. When the stretched band is held in the air for a few seconds, allowed to contract, and then quickly touched to the forehead, there is a noticeable cooling. A rubber strip stretched by means of a mass of about 150 g is gently seated on an electronic balance so that about 20 g of its mass is registered. When a high intensity lamp warms the strip, an apparent mass decrease of several tenths of a gram occurs in the course of about 45 seconds. This indicates that the stretched rubber contracts upon heating—a surprising result.

Answers to Questions

1. Stretching rubber is not spontaneous; ΔG must have a positive value. When the rubber is released, it spontaneously contracts; ΔG is negative. The expression "unstretched $\rightleftarrows$ stretched" should be labeled: from unstretched to stretched is non-spontaneous, from stretched to unstretched is spontaneous.
2. Intermolecular attractions get stronger when rubber is stretched.
3. The contraction of rubber is endothermic, which is unfavorable for spontaneity. Entropy must increase; ΔS is positive. The process is driven by the increase in entropy that occurs as the molecular chains in rubber get more disordered when unstretched.

Additional Activities and Demonstrations

1. Nash, Leonard K. Entropy and Rubbery Elasticity; *J. Chem. Educ*. **1979**, *56*, 363.
2. Smith, Douglas D. Le Châtelier's Principle Demonstrated with a Rubber Band; *J. Chem. Educ*. **1977**, *54*, 701.
3. DeLorenzo, Ronald. Le Châtelier's Principle and a Rubber Band; *J. Chem. Educ*. **1973**, *50*, 124.
4. Laswick, Patty Hall. Entropy and a Rubber Band; *J. Chem. Educ*. **1972**, *49*, 469.
5. *Hands-On Activities: Fun with Chemistry*; Order Number 91-008; Institute for Chemical Education: Madison, WI, 1991. (Available from ICE, University of Wisconsin–Madison, Department of Chemistry, 1101 University Ave., Madison, WI 53706-1396.)
6. Dole, Malcolm. Linear Polymers and Statistics. A Laboratory Experiment; *J. Chem. Educ.* **1955**, *32*, 202–205.

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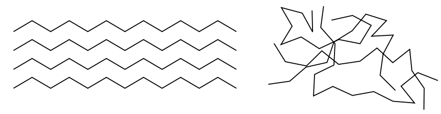
All of us use rubber bands. This Activity reveals some remarkable properties of these familiar objects. Rubber molecules are polymers (large molecules with repeating units) with long hydrocarbon chains. The elasticity of rubber is a consequence of the different degrees of order of these chains in the stretched and unstretched states. Models of the hydrocarbon chains in these two states are shown. In which state do the molecules appear less orderly?



Molecules in a rubber band, stretched (left) and unstretched (right).

In changing between the stretched and unstretched states, a change in *entropy* occurs. Entropy is a measure of molecular disorder. When molecular disorder increases, the entropy change, ΔS, is positive. Energy is also exchanged with the environment when there is a change from one state to the other. When energy is transferred by heating the environment during a process at constant pressure, the process has a negative *enthalpy* change, ΔH. Processes that occur spontaneously (that is, without a constant supply of energy from an external source) are favored by a release of heat to the environment and increased entropy as shown in the Gibbs equation: $\Delta G = \Delta H - T\Delta S$, where ΔG is the Gibbs free energy, T is the Kelvin or absolute temperature, ΔH is the enthalpy change, and ΔS is the entropy change. For a process to occur spontaneously at constant temperature and pressure, ΔG must be negative.

Le Châtelier's principle is also a useful tool in predicting changes. It states that when a stress is applied to a system in equilibrium, the equilibrium will shift so as to relieve the stress.

Try This

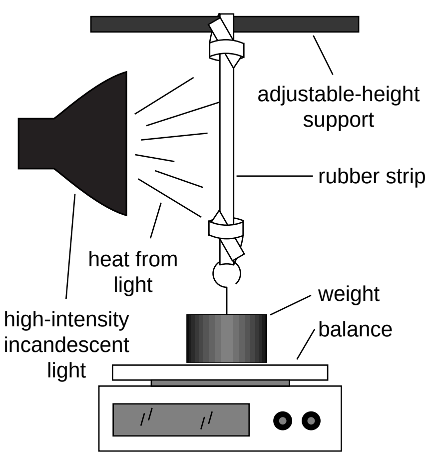
You will need: large rubber band about 8 cm long by 0.5 cm wide; strip 10 cm long by 0.5 cm wide cut from a similar rubber band; scissors; lamp with high-intensity incandescent bulb; digital balance accurate to at least 0.1 g; ring stand; clamp fastener; weight with a mass of about 150 g (an ordinary combination lock will do if such a weight isn't available); clock.

__1. Touch an unstretched rubber band against your forehead for a few seconds and then remove it. Now hold it close to your forehead, stretch it until it is about three times its original length, and *quickly* touch it to your forehead. Note any temperature change. Repeat the steps several times, if necessary, until you are certain of the results.

__2. Stretch a rubber band so that it is about three times its original length and hold it in the air for about 20 seconds. Now let it contract carefully and *quickly* touch it to your forehead. Note any temperature change.

__3. Using Le Châtelier's principle, predict what effect the stress of heating will have on a stretched rubber strip.

__4. Cut a strip 10 cm long by 0.5 cm from a rubber band. Tie one end to a clamp fastener and the other to a weight that has a mass of about 150 g. Attach the clamp fastener to a ring stand. Adjust the height of the clamp so that the weight rests on an electronic balance, with a registered mass of approximately 20 g. When the balance reading stabilizes, record it.



Experimental setup for steps 4 and 5.

__5. Bring a high-intensity incandescent light bulb as close as possible to the rubber strip without touching and turn it on. Record any mass changes for about 45 seconds. Do your observations support your prediction in step 3? How?

Questions

__1. Since a rubber band does not stretch itself, what can you say about the spontaneity of the stretching and releasing processes? About the values for the free energy change (ΔG) for these processes? Write the words "spontaneous" and "non-spontaneous" above or below the appropriate arrows in the expression "unstretched $\rightleftarrows$ stretched".

__2. Bond formation or the strengthening of intermolecular attractions leads to exothermic (heat-releasing) processes. Based on your observations in step 1, what happens to the strength of the intermolecular attractions between neighboring rubber molecules when the rubber band is stretched?

__3. During spontaneous contraction of a rubber band is ΔH (enthalpy change) favorable or unfavorable for spontaneity? In order for spontaneous contraction to occur, what must be true about ΔS (entropy change) and its value? How is your answer related to the molecular structure of rubber when it is stretched and unstretched?

Information from the World Wide Web *(accessed December 2001)*

1. Elastomers; *http://www.psrc.usm.edu/macrog/elas.htm.*