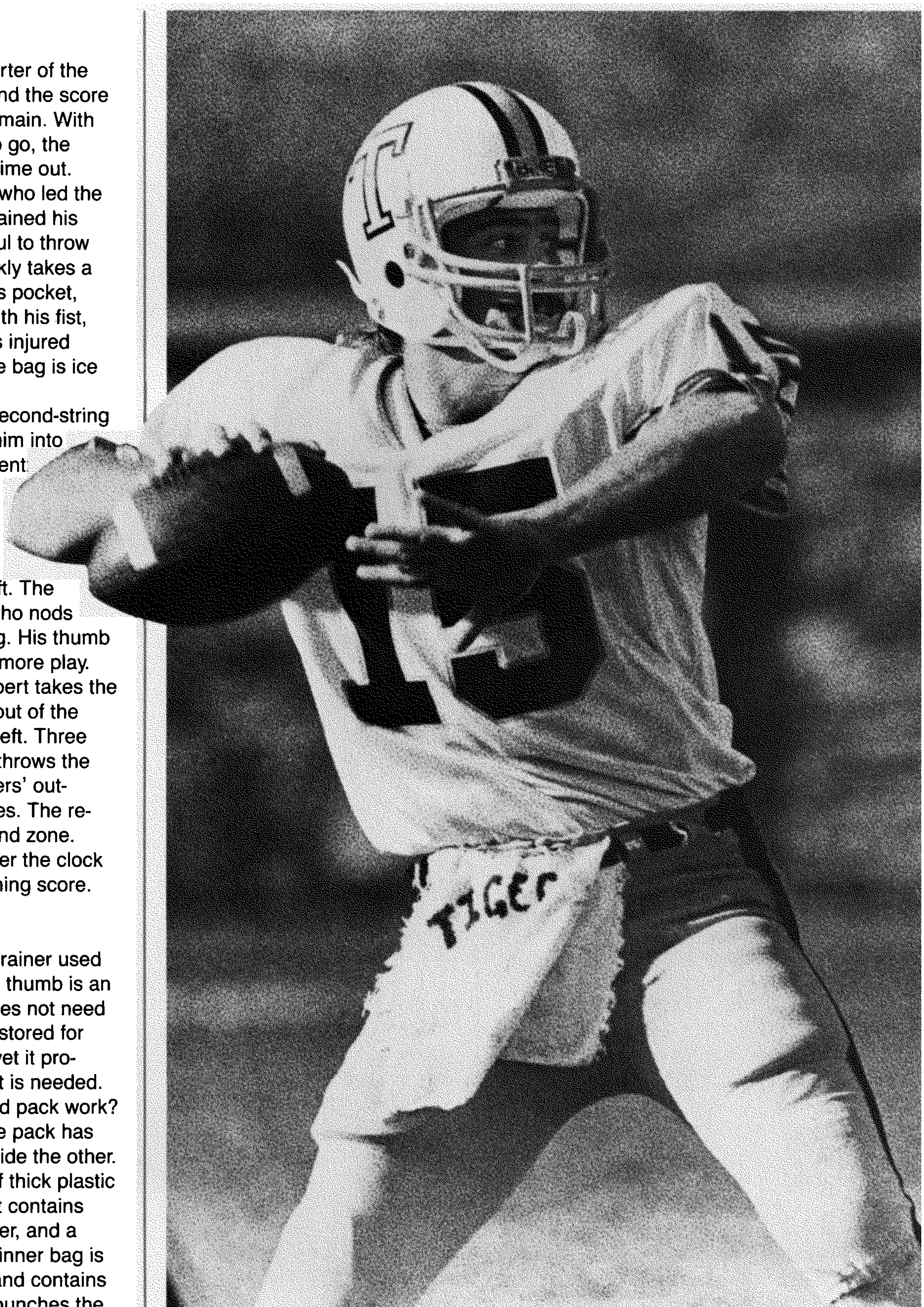
# HOT & COLD PACKS

*by Gail Marsella*




It is late in the fourth quarter of the football championship, and the score is tied. Thirty seconds remain. With second down and goal to go, the home team calls its last time out. Robert, the quarterback who led the team all season, has sprained his thumb, and it's too painful to throw the ball. The trainer quickly takes a white plastic bag from his pocket, gives it a sharp punch with his fist, and applies it to Robert's injured hand. Within seconds the bag is ice cold.

The coach briefs the second-string quarterback and sends him into the game. The replacement calls a pass play, but is sacked even before he can raise his arm to throw. Third and goal to go . . . fifteen seconds left. The coach looks at Robert, who nods and drops the plastic bag. His thumb is numb enough for one more play.

Back in the game, Robert takes the snap, fakes right, steps out of the pocket, then runs to his left. Three defenders rush him. He throws the ball, missing the defenders' outstretched hands by inches. The receiver catches it in the end zone. Touchdown! Seconds later the clock runs out . . . it is the winning score.

## Cold in a bag

The plastic bag that the trainer used to cool the quarterback's thumb is an "instant cold pack." It does not need refrigeration and can be stored for months in a first aid kit, yet it produces cold the moment it is needed. How does the instant cold pack work? As shown in Figure 1, the pack has two sealed bags, one inside the other. The outer bag is made of thick plastic and is relatively strong. It contains two things: a white powder, and a second plastic bag. The inner bag is made of weaker plastic and contains water. When the trainer punches the

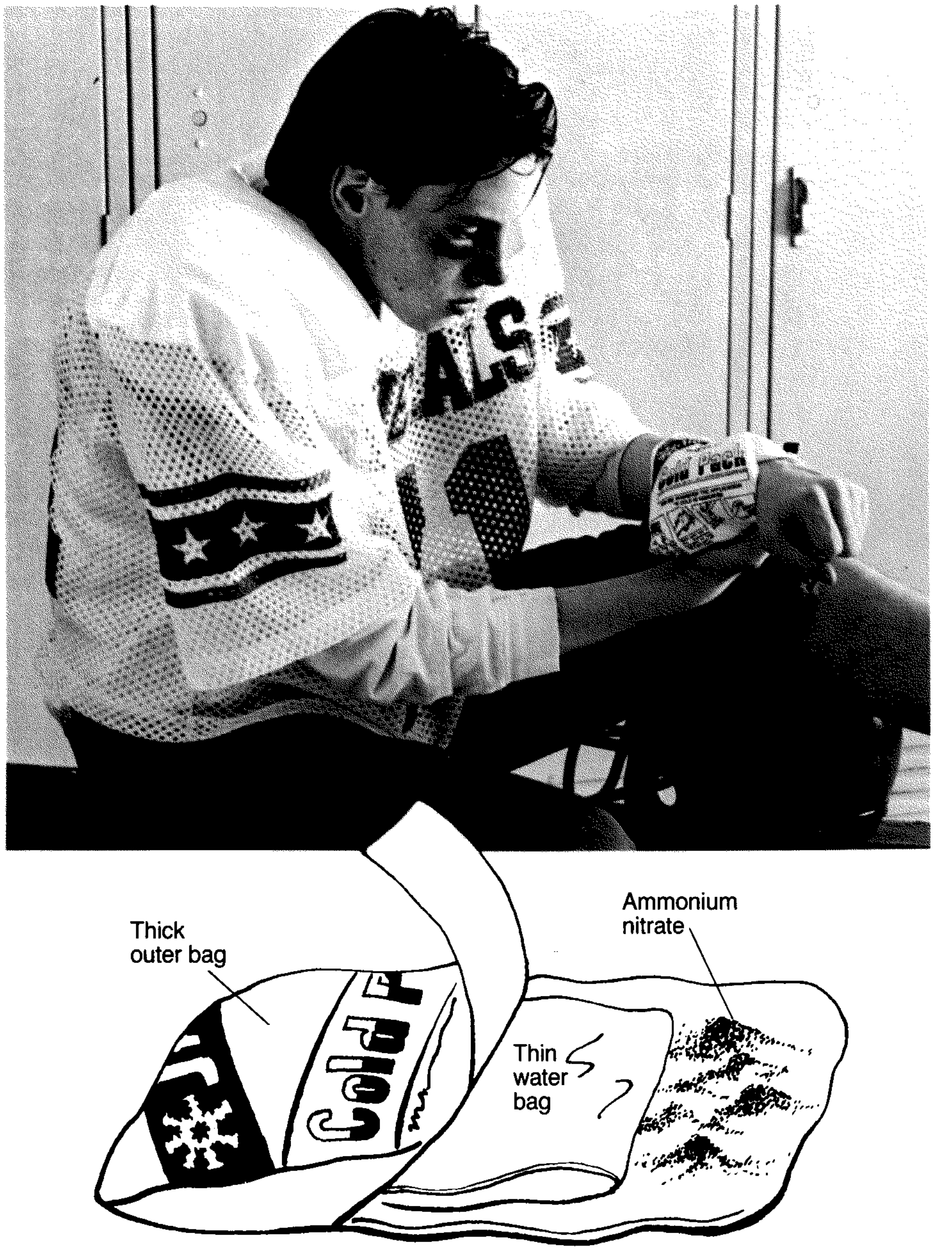



***Figure 1.* Jack Frost brand instant cold pack. The ammonium nitrate crystals and a plastic bag of water are contained inside a heavier plastic bag. Punching the pack bursts open the inner bag, allowing the water and ammonium nitrate to mix.**

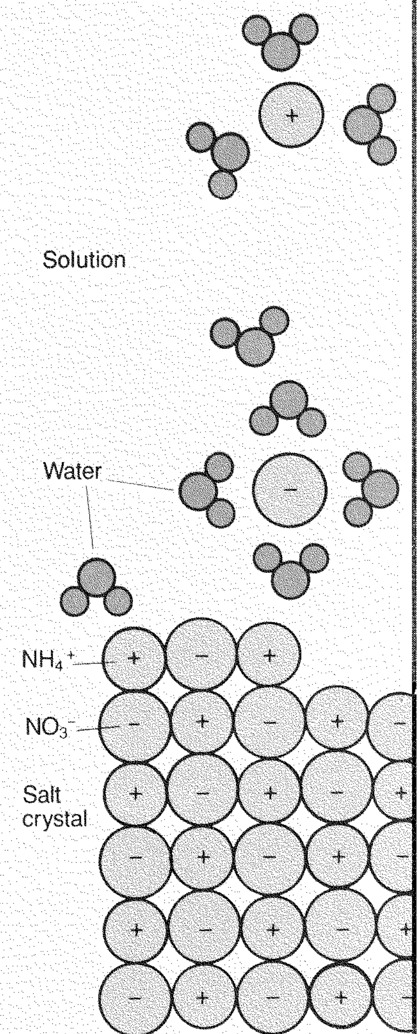
pack the inner bag breaks, and the water mixes with the powder. As the water dissolves the powder—a substance called ammonium nitrate—the solution becomes very cold. The reaction couldn't be simpler: a powder dissolving in water. This particular dissolving reaction absorbs heat, which is a technical way of saying it gets cold. (For *why* it gets cold, see "The cold facts"). Other compounds that get cold on dissolving in water are potassium nitrate, potassium chloride, and, to a very slight extent, plain old table salt (sodium chloride). Some other salts, such as sodium hydroxide, give off heat on dissolving. A reaction that absorbs heat is called an *endothermic* reaction, whereas heat-producing reactions are called *exothermic.*

## Hot stuff

Most familiar chemical reactions give off heat. Light a match. Hot, isn't it? Where does the heat energy come

### The cold facts

Ammonium nitrate ($NH_4NO_3$), is classified as a salt. Chemically speaking, there are thousands of salts in addition to sodium chloride, common table salt. Salts contain ions, particles with electrical charges. Because the ions with positive charge are strongly attracted to those with negative charge, they form a solid crystal. Below is a diagram of a salt crystal dissolving in water. To the eye, it looks like a simple process. In fact, there are two distinct steps, and each involves energy changes. In the first step, the solid crystal separates into ions. Breaking the ionic bonds requires a lot of energy, which means that heat must be absorbed from the surroundings. In the second step the water molecules, which are attracted to the

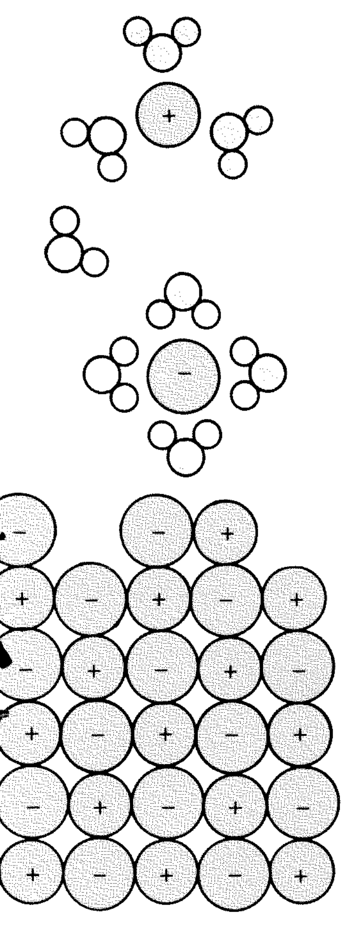


charged ions, attach themselves to the ions. This step releases energy, which means that heat flows to the surroundings. The steps can be written like this:

*Step 1:*
$NH_4NO_3$ + Heat $\rightarrow NH_4^+ + NO_3^-$

*Step 2:*
$NH_4^+ + NO_3^- + H_2O \rightarrow$
$NH_4^+ (H_2O)_x + NO_3^- (H_2O)_x$ + Heat

Several water molecules may bond to each ion, as indicated by $(H_2O)_x$. In the first step, heat is absorbed; in the second step, heat is released. Overall, because more heat is involved in the first step than in the second step, heat is absorbed from the surroundings (6 kilocalories per mole of ammonium nitrate). This leaves the surroundings with less thermal energy—colder.



from? It wasn't in the match before you struck it, was it?

Yes it was. It was *stored* in the match—in the various chemicals that make up the match. When the match burned, a series of vigorous reactions took place. Combustion occurs in many steps. To break the original bonds, heat must be absorbed. As new bonds are formed, heat is released. In this case, the amount absorbed is less than the amount released. Overall, heat is given off—the surroundings get hot.

Not all exothermic reactions are as vigorous as a burning match. Instant hot packs use slower reactions that take place at lower temperatures. The "Heat Factory" is a brand of hot pack that is sold at many camping stores. It has an outer plastic envelope and an inner paper bag perforated by minute holes (see Figure 3). The paper bag contains a mixture of powdered iron,

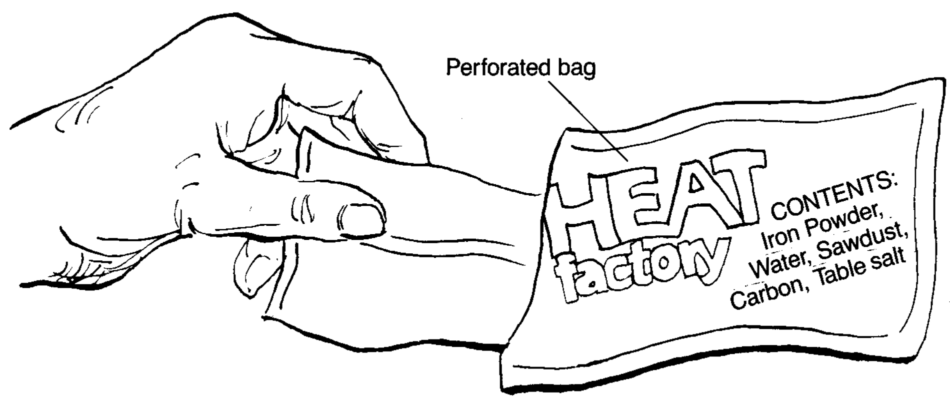



***Figure 2.* An instant heat pack. Remove the inner bag from the plastic envelope and shake it to start the heat-releasing reaction. Because the reaction needs oxygen from the air, you can stop it by returning it to the airtight envelope, then restart it later.**

sodium chloride, activated charcoal, and sawdust, all dampened with water. Remove the envelope from the outer plastic bag and shake it vigorously. It gets hot! What's going on here?

Everyone knows what happens when an iron shovel is left out in the rain for a couple of days—it rusts. The chemical reaction of iron and oxygen (oxidation), produces iron (III) oxide, or rust.

$$4Fe + 3O_2 \rightarrow 2Fe_2O_3 + \text{Heat}$$

In this reaction, ionic bonds are formed between iron and oxygen and heat is released (197 kilocalories per mole of iron (III) oxide). The rusting goes faster if the iron is wet, and faster still if the iron is wet with a salt solution. The shovel left out in the rain rusts too slowly for the heat to be noticeable. In the Heat Factory, though, the ingredients are mixed in precise proportions and ground up finely to make the oxidation go much faster. The Heat Factory is activated by shaking the envelope to get the oxygen in the air circulating through the small holes. The heat is the result of fast rusting.

Another brand of heat pack, called the "Heat Solution," works on a different principle. The Heat Solution looks like a small air mattress and is filled with a liquid the consistency of honey (see Figure 3). To activate it, you squeeze a special compartment in one corner of the pack, which releases a triggering crystal. The liquid then gradually solidifies and gives off heat for several hours.

This heat generator uses a *phase change* instead of a chemical reaction. We are all familiar with the three common phases of matter: solid, liquid, and vapor. The most common example is water, which can exist as ice, liquid water, or steam—same chemical, different phases. Like other substances, water has specific temperatures at which it changes

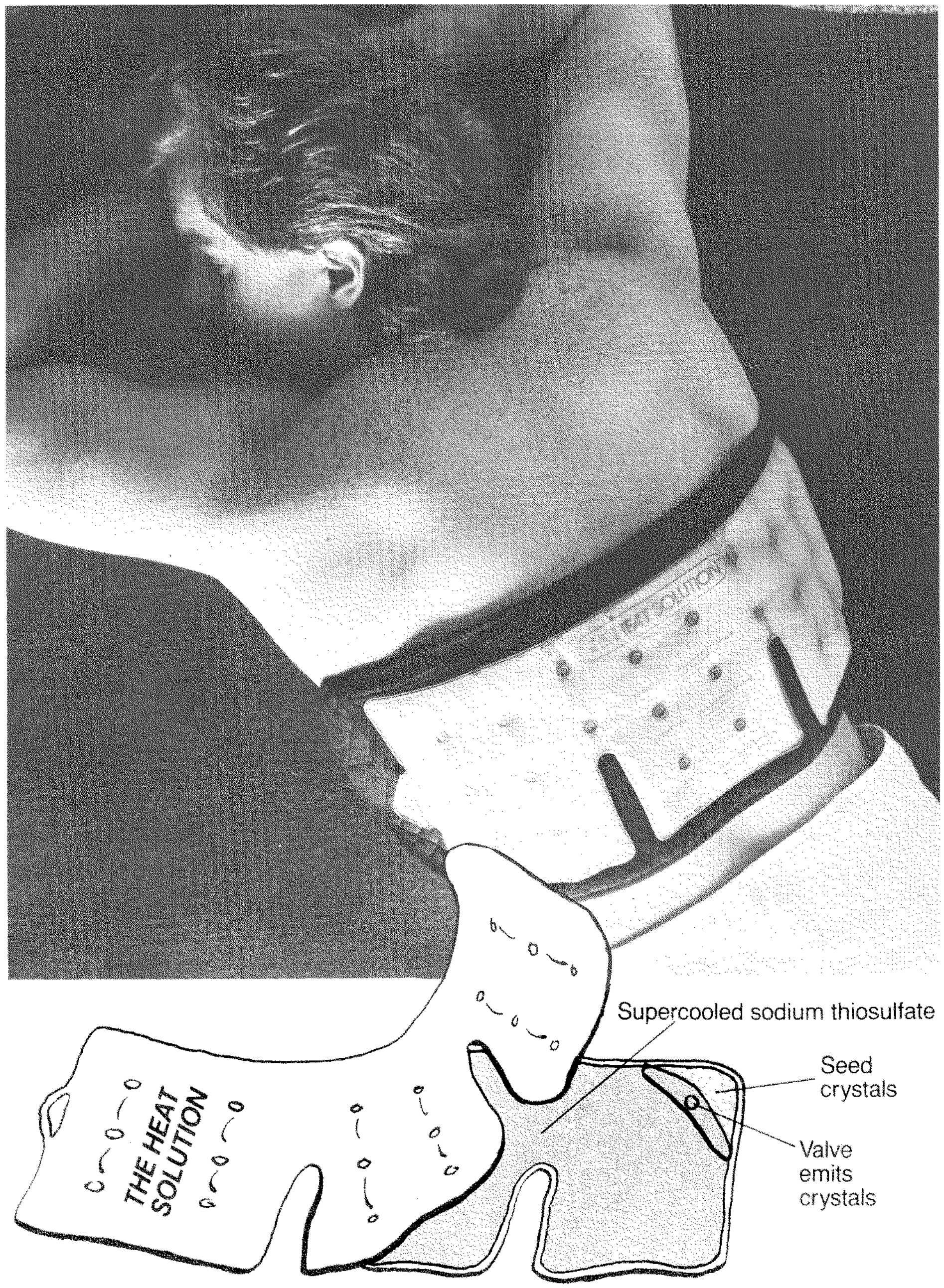



*Figure 3.* **A constant-temperature heat pack. A triangular pocket contains seed crystals that can be released through a valve by squeezing the corner. This triggers the crystallization that warms the pack and maintains a comfortable 48 °C (118 °F).**

phase—boiling point (100 °C) and freezing point (0 °C).

Under certain conditions, a phase can exist outside of the normal temperature limits. Water, for example, can be cooled below 0 °C. Meteorologists have learned that, high in the atmosphere, the tiny droplets of water in clouds may be as cold as −30 °C and still be liquid. When a chemical remains liquid at temperatures below its normal freezing point, it is called a *supercooled* liquid.

What does this have to do with hot packs? The liquid in the Heat Solution contains supercooled sodium thiosulfate. To make the supercooled liquid solidify, a *seed crystal* is needed. This is simply a small piece of solid sodium thiosulfate around which more solid can crystallize. When a seed crystal is added, it triggers the change from supercooled liquid to solid. As the sodium thiosulfate solidifies around the seed crystal, the pack heats up. The heat is the result of bonds being formed as the substance crystallizes. The temperature rises to the freezing point of the sodium thiosulfate, a pleasingly warm 48 °C (118 °F). The valuable feature of phase change systems is that they can't overheat. When a supercooled substance crystallizes, the temperature rises to the freezing point and stays there. It goes no higher or lower until all of the material has solidified. Notice that the inventors picked their chemical carefully. Unlike many compounds that cannot be supercooled at all, sodium thiosulfate supercools easily, and its freezing point is comfortably warm, but not hot enough to burn the person who has a pulled muscle.

Unlike the other hot or cold packs, the Heat Solution is reusable. Simply heat the pack in boiling water for a while to return the sodium thiosulfate to its supercooled state; let it cool, and it's ready for the next emergency. The pack can be recycled until the supply of seed crystals is used up. (A home-made heat pack is described in "Experimenter's Notebook," page 12.)

### The tendency to mess up

Portable hot and cold packs depend on reactions that are *spontaneous.* Because the packs must be quick and easy to use, they require reactions that begin as soon as the reactants are placed together and that will continue on their own. Most spontaneous chemical reactions are exothermic—they give off heat. This is because chemical bonds have a tendency to shed their stored energy and release it as heat. The people who designed hot packs found that this natural flow of energy suited their needs perfectly. They selected the appropriate reactants, put them in the same package, but kept them separated. When warmth is needed, the reactants are simply mixed, and heat is produced automatically.

The tendency of stored bond energy to emerge as heat would seem to rule out cold packs. Because endothermic reactions absorb heat, the bonds end up with more stored energy than they started with—which is against the natural flow of things. Yet, this occasionally happens. When ammonium nitrate dissolves in water it gets very cold—spontaneously. Why does this occur? Scientists explain it with a concept called *entropy.*

Entropy is the degree of disorder in a system. Chemical changes tend to go from orderly arrangements of molecules and ions to disorderly arrangements. Nature tends to increase the amount of messiness, or disorder, or entropy.

The natural tendency to increase entropy sometimes opposes the tendency to release heat. When the increase in entropy is great enough, it can drive the heat flow "backward." The drive for high entropy overpowers the drive to release heat. Endothermic reactions happen spontaneously *only* when the reaction permits a large increase in entropy.

In the case of the instant cold pack, the starting materials were highly ordered: The water was pure and sealed in its own container, and the ammonium ions and nitrate ions were arranged in an orderly pattern in solid crystals. The substances were sorted and organized—everything in its place. When the inner plastic bag was broken and the water dissolved the ammonium nitrate, the orderly arrangement of the ions was disrupted. The ions were dispersed randomly throughout the water, and the once-pure water became "contaminated." Disorder reigned. The system went from very ordered to very disordered, and the reaction was partly driven by this increase in entropy.

## Bond energy

We have examined three thermal first-aid packs. The instant cold pack uses a dissolving reaction (ammonium nitrate in water) that is endothermic. The Heat Factory uses an exothermic chemical reaction (iron and oxygen rust to iron (III) oxide). The Heat Solution uses an exothermic phase change (crystallization of supercooled sodium thiosulfate). Only in the Heat Factory "fast-rust" system was a new chemical compound formed. Nevertheless, the underlying theory is the same. Chemical processes always involve breaking and making bonds, which cause heat to be absorbed and released. It is the relative balance of heat change that determines whether the overall process feels hot or cold to the touch.

It is a week after the football game. Having won the championship, Robert and some friends are on a weekend camping trip. They had planned a lot of fishing but, at the lake, they mostly talk about the game, eat, tell jokes, and relax. What if it gets cold during the night, and the fire won't start? What if one of them strains a muscle chopping wood? Robert is not worried. In addition to the food, tents, and sleeping bags, he brought some chemical hot and cold packs.

***Gail Marsella*** teaches chemistry at Muhlenberg College, Allentown, Pa.

### References

Mortimer, Charles. *Chemistry,* 6th ed.; Wadsworth Publishing: Belmont, Calif.

"Exothermic Composition and Warming Bag Containing Same," U.S. Patent 4,268,272, May 19, 1981.

"Constant Temperature Device," U.S. Patent 3,951,127, April 20, 1976.

"Refrigerating Package," U.S. Patent 2,925,719, February 23, 1960.

Shakhashiri, Bassam Z. *Chemical Demonstrations: A Handbook for Teachers of Chemistry;* University of Wisconsin Press: Madison, Wis., 1983, Vol. 1.