The following is taken from the book *The Second Law*, by Henry A. Bent (Oxford University Press, New York, 1965) first edition, p.22ff. The material in quotes was taken from *Harvard Case Histories in Experimental Science, Vol. I*, James B. Conant, ed., 1957. Copyright 1957 by the President and Fellows of Harvard College.

Joseph Black and the Melting of Ice

The magnitude of the energy changes that occur in the universe when ice melts was not appreciated until the experiments of an Englishman, Joseph Black (1728-99). The motivation behind these experiments, their nature, and their chief results, are described in Dr. Black's own words (with some modernizations) in the following paragraphs.

"Our experience of freezing of liquids when exposed to more or less powerful degrees of cold is almost universal. The exceptions are very few. The strongest spirit of wine and a few subtle and volatile oils are the only substances that have not yet been solidified by any degree of cold hitherto known. ... Quicksilver was, not long since, one of this small number of substances, which having never been seen in any other than a liquid state, was considered as naturally and essentially liquid, and incapable of being reduced to a solid form, until experiments were made with it, first in different parts of the Russian Empire, since the year 1760, and verified afterwards in other places. By these experiments, every person must be convinced that quicksilver is a metal that can become solid and malleable like the rest, but that it freezes at a lower temperature than has ever been observed over the greater part of the surface of this earth. In the same manner may we consider all other liquids as solids melted by heat.

Some philosophers, however, have offered many objections to this general proposition concerning the nature of liquids. They thought it necessary to suppose that water is an exception. They could not be persuaded that its liquidity is the effect of heat, but supposed this quality to be an essential one of the water, depending on the spherical form and polished surface of its particles, and that the freezing of it depended on the introduction of some extraneous, subtle matter. ...

The propensity of many people to imagine water as naturally and essentially liquid is a prejudice contracted from the habit of seeing it much oftener in this state than in the solid state. ...

In considering the effect of heat in producing liquifaction, we should first remark that innumerable experiments made with thermometers show that the change of a particular substance from solid to liquid occurs only when the temperature is increased to a certain value. Above this temperature the substance is a liquid. If the liquid is cooled back down to this temperature, it becomes solid, and it remains solid at all lower temperatures. This at least may be stated as the general fact. ...

In general, each different kind of matter must be heated to a particular temperature to render it liquid, and below this temperature it is either solid or has some degree of solidity (beeswax, resin, tallow, glass, etc.). This temperature is therefore called the FREEZING or the MELTING POINT of the substance. It is called the freezing point of such substances as exist commonly in the liquid state, and the melting point of those that are solid under ordinary circumstances. ...

I must now add that the foregoing account of liquefaction as an effect of heat is not complete and satisfactory. ...

Melting had been universally considered as produced by the addition of a very small quantity of heat to a solid body, once it had been warmed up to its melting point. ...

This was the universal opinion on the subject, so far as I know, when I began to read my lectures in the University of Glasgow in the year 1757. But I soon found reason to object to it, as inconsistent with many remarkable facts, when attentively considered. ...

The opinion I formed from attentive observation of the facts and phenomena is as follows. When ice or any other solid substance is melted, I am of the opinion that it receives a much larger quantity of heat than what is perceptible in it immediately afterwards by the thermometer. A large quantity of heat enters into it, on this occasion, without making it apparently warmer, when tried by that instrument. ...

On the other hand, when we freeze a liquid, a very large quantity of heat comes out of it, while it is assuming the solid form, the loss of which heat is not to be perceived by the common manner of using the thermometer. ...

If we attend to the manner in which ice and snow melt when exposed to the air of a warm room, or when a thaw succeeds to frost, we can easily perceive that, however cold they might be at first, they soon warm up to their melting point and begin to melt at their surfaces. And if the common opinion had been well founded – if the complete change of them into water required only the further addition of a very small quantity of heat – the mass, though of a considerable size, ought all to be melted within a very few minutes or seconds by the heat incessantly communicated from the surrounding air. Were this really the case, the consequences of it would be dreadful in many cases; for, even as things are at present, the melting of large amounts of snow and ice occasions violent torrents and great inundations in the cold countries or in the rivers that come from them. But, were the ice and snow to melt suddenly, as they would if the former opinion of the action of heat in melting them were well founded, the torrents and inundations would be incomparably more irresistible and dreadful. They would tear up and sweep away everything, and this so suddenly that mankind would have great difficulty in escaping their ravages. This sudden liquefaction does not actually happen. ...

In order to understand better this absorption of heat by the melting ice, and concealment of it in the water, I made the following experiments. ...

I chose two thin globular glasses, 4 inches in diameter, and very nearly the same weight, I poured 5 ounces of pure water into one of them, and then set it in a mixture of snow and salt until the water was frozen into a small mass of ice. It was then carried into a large empty hall, in which the air was not disturbed or varied in temperature during the progress of the experiment. ...

I now set up the other globular glass precisely in the same way, and at the distance of 18 inches to one side, and into this I poured 5 ounces of water, previously cooled almost to the freezing point-actually to 33°F. Suspended in it was a very delicate thermometer, with its bulb in the center of the water, and its stem so placed that I could read it without touching the thermometer. I then began to observe the ascent of this thermometer, at suitable intervals, in order to learn with what celerity the water received heat; I stirred the water gently with the end of a feather about a minute before each observation. The temperature of the air, examined at a little distance from the glasses, was 47°F.

The thermometer assumed the temperature of the water in less than half a minute, after which, the rise of it was observed every 5 to 10 minutes, during half an hour. At the end of that time, the water was 7 degrees warmer than at first; that is, its temperature had risen to 40°F.

[Dr. Black next explains that the time to warm the ice-containing glass to 40°F was 10 hours.]

It appears that the ice-glass had to receive heat from the air of the room during 21 half-hours in order to melt the ice and then warm the resulting water to 40°F. During all this time it was receiving heat with the same celerity (very nearly) as had the water-glass during the single half-hour in the first part of the experiment. ... Therefore, the quantity of heat received by the ice-glass during the 21 half-hours was 21 times the quantity received by the water-glass during the single half-hour. It was, therefore, a quantity of heat, which, had it been added to liquid water, would have made it warmer by (40 -33) x 21, or 7 x 21, or 147 degrees. No part of this heat, however, appeared in the ice-water, except that which produced the temperature rise of 8 degrees; the remaining part, corresponding to 138 to 140 degrees, had been absorbed by the melting ice and was concealed in the water into which it was changed."