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RUBBER ELASTICITY IN THE INTRODUCTORY THERMODYNAMICS COURSE*

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Abstract

An experimental set-up is described in which the temperature of a piece of rubber is measured with thin wire thermocouples. It measures and records the temperature change of the rubber as it heats and cools in response to elongation and contraction. This mechano-caloric effect arising from the entropy elasticity of rubber represents a reversible thermal process in clear distinction from most of other heat effects encountered in our daily experience where the irreversibility is inevitably involved. The demonstration experiment has been proved useful in elementary thermodynamic courses for introducing the entropy concept.

Keywords: entropy, mechano-caloric effect, rubber elasticity, thermodynamic reversibility

Introduction

Many of us who teach thermodynamics courses will agree that entropy is the most difficult concept in introductory physical chemistry. It is also profound. One reason for the difficulty we have in understanding the entropy is that we rarely, if ever, encounter in our daily experience a process in which the heat is transferred reversibly. We see irreversible transfer of heat (e. g., a kettle heated by burning gas) from which we learn about the first law, but not the second law.

The difficulty is also apparent in the formulation of the thermodynamics lectures. In one of the established formulations, the second law is introduced in the form of the Clausius inequality.

$$\Delta S \geq \Delta Q/T \tag{1}$$

Irreversibility and reversibility are represented by the inequality and equality parts of this expression, respectively. After a short discussion of irreversibility, usual thermodynamics lectures proceed on with derivation of numerous thermodynamic

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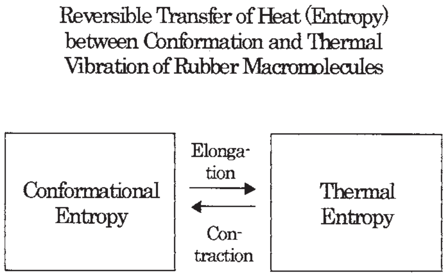

Fig. 1 Thermal effects accompanying elongation and contraction of rubber

equations all based on the equality part of the Clausius inequality. The inequality part is seldom mentioned, while it is stressed at the beginning that a real process is always irreversible.

It will be helpful both to the students and teachers in this situation if we have a process in which the entropy is conserved and which can be shown to the students in introductory thermodynamics courses. In this paper we describe an experiment for demonstration in a thermodynamics course in which the temperature of a piece of rubber is measured and recorded on a strip chart recorder. By stretching the rubber to a suitable tension and releasing it a short time after, one records an increase of the temperature in the first process and a closely matching decrease in the second process. Because of the reversibility, the process is called a mechano-caloric effect following the general way of word formation. The physical mechanism underlying the temperature change is that the entropy is transferred from the conformation of the rubber macromolecules to their thermal vibration when the rubber is stretched and in the opposite way when it is allowed to shrink (Fig. 1) [1].

Experimental

The experimental set-up is shown in Fig. 2. The apparatuses and minor items needed for the experiment are as follows.

1. A circular rubber band, diameter 70 mm, width 12 mm, thickness 1 mm.
2. Two metallic clips (a stationery item) and two pieces of copper wire, 1.5 mm diameter.
3. A laboratory stand, 80 cm high, and a few screw clamps. These are not shown in Fig. 2.
4. A spring balance, 5 kg.
5. A ruler, 50 cm.
6. A copper–chromel–constantan–copper thermocouple. The chromel–constantan part is 0.1 mm in diameter and nylon coated, length 100 cm. The reference junctions (copper–chromel and constantan–copper) are fixed to a piece of metal with adhesive tape. It is not necessary to put them in an ice bath.

7. A microvolt amplifier with an output signal available for recording.
8. A strip chart recorder.
9. Three blank OHP sheets.

The two items 7 and 8 may be replaced with a digital voltmeter and a personal computer.

The rubber band is folded into a parallel pair of sheets and its upper and lower ends are caught between the jaws of the clips. The copper wire pieces are inserted through the folded rubber ring and formed into rings at its upper and lower ends. The ring on the upper end is fixed to the top of the laboratory stand while the one on the lower end is attached to the spring balance. The thermocouple junction is inserted between the folded sheets of the rubber band. The position of the thermocouple is important for successful operation of the experiment. It should be about 10 mm below the upper clip. This ensures the thermocouple junction to remain between the rubber sheets, thanks to the elasticity of the rubber, when it is stretched as well as when it is released. The short distance 10 mm is also important because a thermocouple junction fixed to the rubber at a longer distance from the clip would result in a larger displacement downwards as the rubber is stretched, which would dislodge the thermocouple junction out of contact with the rubber.

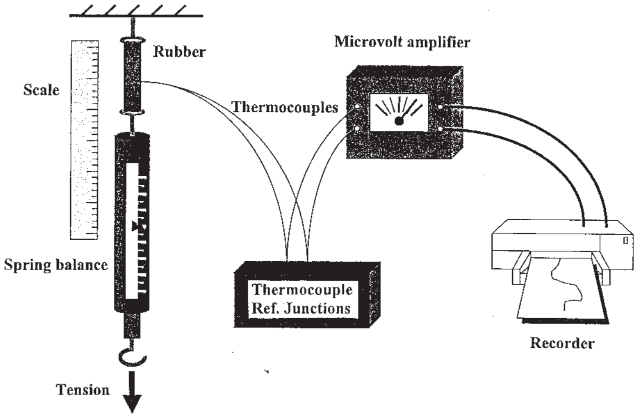

Fig. 2 Schematic diagram of the experimental set-up for recording the mechano-caloric effect in rubber

Two blank OHP sheets are pieced together with adhesive tape to form a cylinder of a 120 mm diameter. One end of the cylinder is closed with a disk cut from the third blank OHP sheet. A hole is punched in the disk. The cylinder is placed at the top of the laboratory stand to cover the rubber. This avoids the airflow that would change the temperature of the rubber erratically. The hole perforated in the end face keeps the cylinder in position at the top of the laboratory stand.

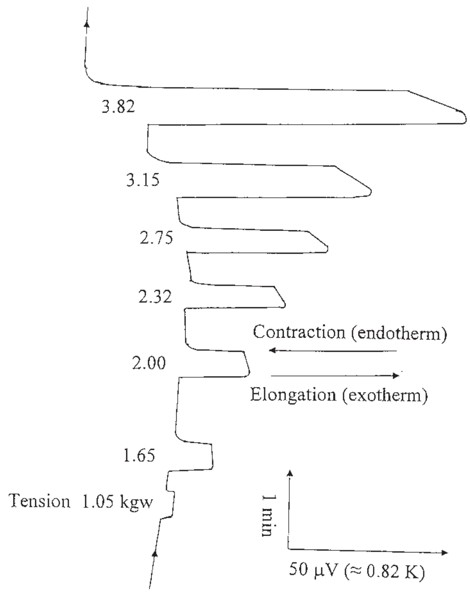

Fig. 3 A recorder trace showing the heating and cooling which the rubber band undergoes as it is stretched and released. The zero line shifted during the experiment but the real effect is easily recognized because of the fast response. A tension of 1 kgW is equal to 9.806 N

When the apparatus has been set up and the temperature stabilized (typically to 10 microvolts in 5 min), the rubber band is stretched by pulling down the spring balance to 3.0 kgW. A screw clamp will be helpful to stop the balance at an elongated position. The temperature will rise rapidly by 1.0 K (about 60 microvolts), the exact number being dependent on the rubber thickness and the heat capacity of the thermocouple relative to that of the rubber. (Hence a thin thermocouple is preferable.) The temperature will decrease to the original value when the rubber is allowed to shrink to the initial length. This shows the reversibility of the heating and cooling. The tension may be changed to obtain a different magnitude of heating. A ruler will be useful for measurement of the elongation *vs*. the tension. A recorder trace is reproduced in Fig. 3 where the heating and cooling of the rubber as it is stretched and released are shown for different tensions. The results are summarized in Figs 4 and 5 as plots of the temperature rise and elongation *vs*. the tension, respectively. A plot of ΔT *vs*. the relative elongation will be also useful.

The temperature change is related to the entropy of the rubber by the following equation.

$$\left(\frac{\partial T}{\partial l}\right)_S = -\frac{\left(\frac{\partial S}{\partial l}\right)_T}{\left(\frac{\partial S}{\partial T}\right)_l} \tag{2}$$

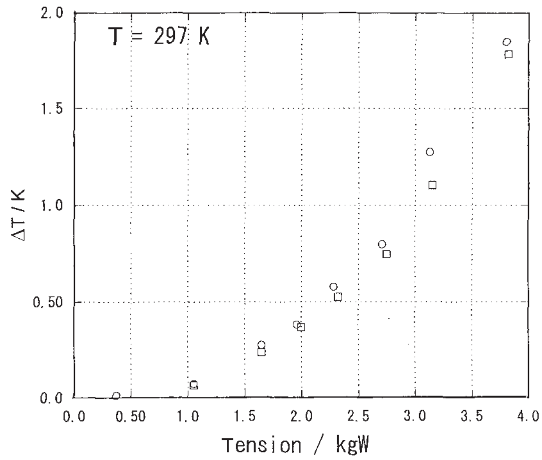

Fig. 4 A plot of the magnitude of the mechano-caloric effect *vs*. the tension

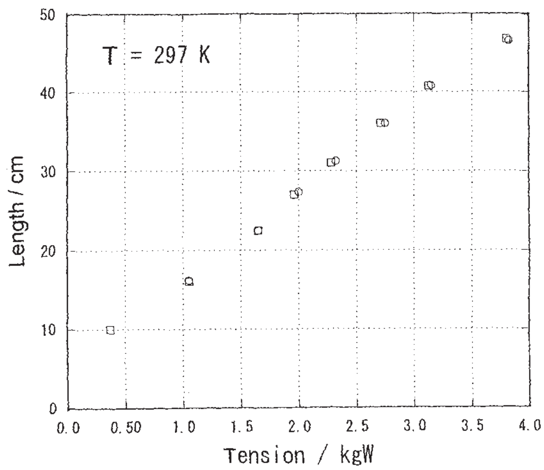

Fig. 5 Relation between the length and tension of the rubber band

S, *T* and *l* are the entropy, temperature and the length of the rubber band, respectively. The numerator on RHS of this equation is negative because a stretched rubber band has a smaller number of available conformations than a free one. The denominator is positive because the heat capacity is always positive. With the negative sign as indicated in the equation, one deduces a positive temperature change for elongation and a negative one for contraction in agreement with the experiment. The comparison may be made semi-quantitative by substitution of suitable numbers in this equation. Effects of crystallization may also have to be included [2, 3].

Discussion and conclusions

The temperature change in a stretched elastic band can be felt by sensitive parts of our skin (lips and cheek) and has been used by instructors in thermodynamics courses. It is shown by the present experiment that the temperature change is reversible to a good approximation. This allows us to talk about 'entropy conservation' in the limited case in hand. It will facilitate the understanding of the Carnot cycle and the entropy itself, with an extra attention paid to the distinction between reversible and irreversible changes.

For thermodynamic investigation of the entropy elasticity itself, more elaborate experiments (e.g., measurement of the tension as a function of length and temperature [4]) under better-controlled conditions are preferable to the present experiment. The present experiment has the merit of being explicit about the reversibility of the temperature change. The reversibility may be traced back to the heating (and cooling) mechanism: the heat evolves and retracts evenly over the volume of the rubber as it is stretched and released, respectively. Thus, conduction of heat over any macroscopic distance (other than the conduction across the interface between the rubber and thermocouple junction) is not involved in the present heating and cooling mechanism. The fast response shown in Fig. 3 is a consequence of this mechanism. In fact the response may surprise the experimenter who would expect a slower temperature change from the poor thermal conductivity of rubber. Also the meaning of an adiabatic process may be learned here: the process should be fast enough to preclude exchange of heat between the rubber and air.

As to the definition of a reversible process as an infinitely slow one that traces a series of equilibrium states, any rapid elongation possible with the present apparatus is slow enough to be quasi-static. In fact it is important to specify the reference by which a process is judged as slow or fast. For the present case the reference will be the rate of the conformation change of rubber macromolecules, for which the relaxation time is less than 1 ms at 300 K.

We have used the present demonstration experiment along with a simpler version (i. e., feeling the temperature on the skin) on several occasions. The response of the students has been invariably positive and has shown that it is useful as a device for providing a basis of a concrete experimental fact on which the students may contemplate more about the entropy.

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