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Very fast versus very slow processes: Which are more efficient (closer to reversibility)?

Contributed by

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Principle

Transfer of electricity out of a storage battery is much more efficient (closer to reversibility) when it is very fast rather than very slow.

Object

It is often argued that reversible processes take an infinite time to complete and, therefore, are of questionable usefulness. Although there is truth in this argument for certain processes, such as transfer of energy across a finite temperature difference, the argument is neither universally valid nor representative of some practical phenomena. A simple and very important counterexample is provided by a storage battery. If discharged quickly, the battery does work almost equal to the stored energy. If discharged more slowly than the rate of its internal discharge (let alone infinitely more slowly), the battery does practically no work, that is, all its availability is dissipated. The availability is dissipated because the internal discharge generates entropy spontaneously or, said differently, the internal discharge is irreversible.

Apparatus

As shown schematically in Fig. 29.1, the apparatus consists of a cell with two electrodes (1), a temperature bath (2), a glass thermometer and an electric heating plate (3), a galvanostat (4), a resistance box (5), an ammeter (6), and a voltmeter (7). Another schematic of the apparatus is shown in Fig. 29.2.

The cell consists of a 3-liter Pyrex beaker that contains two liters of sulfuric acid aqueous electrolyte and two lead electrodes. The density of H_2SO_4 is 1.28 g/cm^3 . The H_2SO_4 solution may be prepared by diluting 660 cm^3 of H_2SO_4 in 1340 cm^3 of water.

Each electrode is made of 5.5-cm-x-6.2-cm-x-0.038-mm (1.5-ml) lead foil. Each foil is sandwiched between two 17-cm-x-7-cm-x-0.6-cm plexiglass frames

with a 5-cm-x-5-cm window at the location of the foil (see Fig. 29.3). Thus, each foil can be held firmly at the desired position. The distance between the electrodes is about 7 cm.

The cell is immersed in a 5-liter beaker filled with water or oil which serves as a temperature bath. The temperature of the bath is controlled by the electric heating plate, and measured by the glass thermometer. Temperatures in the range 20 °C to 60 °C are used.

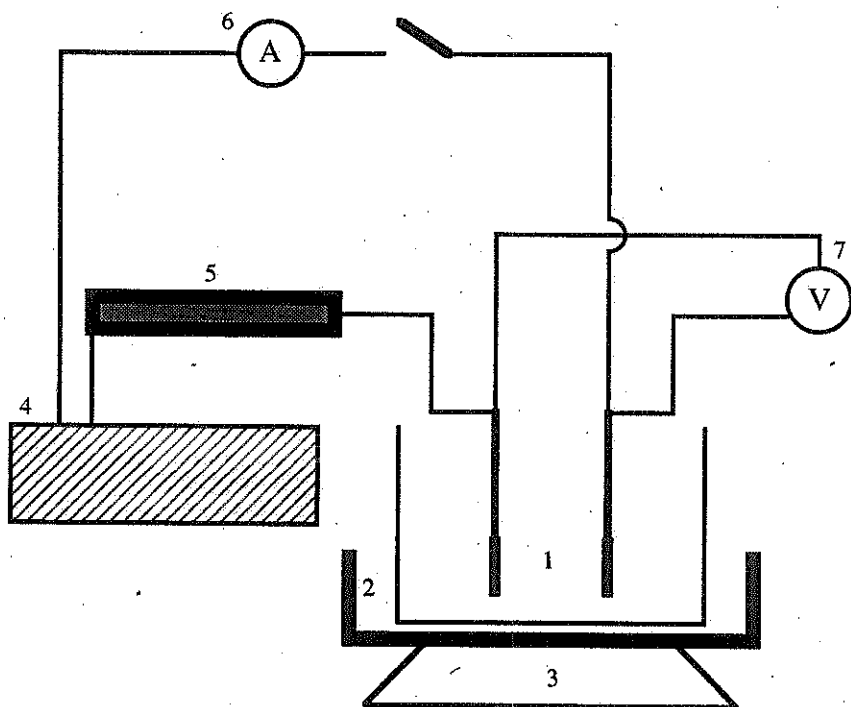
The galvanostat is model AMEL #549, and supplies direct current up to 1000 mA. The resistance box provides a resistive load in the range from 1 to 10⁵ ohms. An ammeter (1 μ A to 2 A) and a voltmeter (1 mV to 1 kV), or two multimeters, are used for current and voltage measurements.

Procedure

The cell is charged by a current $I = 750$ mA for 30 minutes. During the charging period the voltmeter reads between 3 and 3.5 volts, and the cell temperature is kept at 25 °C.

Two procedures are used for the discharge experiments. In the first, the work-producing procedure (WP), the cell is discharged through a resistive load in the range between 200 and 2000 ohms.

Fig. 29.1. Schematic of experimental apparatus: (1) cell; (2) water bath; (3) heating plate; (4) galvanostat; (5) resistance box; (6) ammeter; (7) voltmeter.

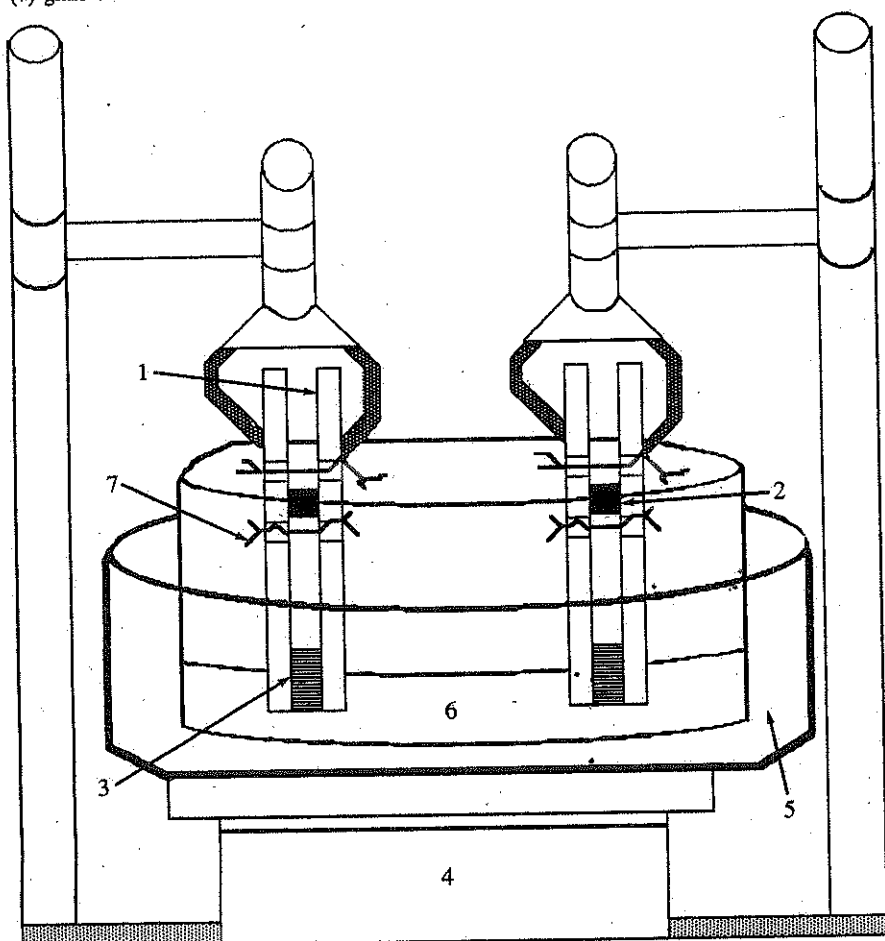


The current I through the load and the voltage V across the load are recorded as functions of time, beginning at the instant the charging phase is interrupted, and lasting until the cell is dead.

A graph of the product $P = I \times V$ versus time is made. It represents the power or work per unit time done by the cell. The integral under the power graph is the work done by the cell.

In the second, the self-discharge procedure (SD), no resistive load is connected at the end of the charging phase, and no work is done by the cell. Only from time to time is the voltage across the cell observed by connecting the electrodes to a large resistor (3000 ohm or larger) for a few seconds. Each self-discharge experiment lasts several hours, until the cell is dead.

Fig. 29.2. Schematic of temperature-controlled electrochemical cell: (1) plexiglass frame; (2) lead contact; (3) lead electrode; (4) heat plate; (5) water bath; (6) sulfuric acid solution; (7) glass container.



Results

Typical experimental results are listed in Table 29.1. The table includes the type of experiment, the temperature of the cell, the resistive load, the length of time of the experiment, and the work done by the cell.

It is clear from these results that, if work is done at a rate faster than that dictated by the rate of self-discharge, the cell does relatively a lot of work. On the other hand, if no work is done (work is done at an almost zero rate), the self-discharge dissipates all the ability of the cell to do work, and no work can be transferred to an external load.

Of course, the reason for the dissipation is the spontaneous generation of entropy in the course of self-discharge, that is, irreversibility.

The data also show that, as temperature increases, the rate of self-discharge increases. The reason is that as temperature increases, internal reaction rates increase.¹

More fundamentally, it is interesting to compare the transfer of energy out of a fixed-volume battery to an electric load, and the transfer of energy out of a fixed-volume, fixed-temperature reservoir to a lower-temperature reservoir. In the former case, the transfer is out of a state that is not a stable

Fig. 29.3. Front (a) and side (b) views of the electrodes.

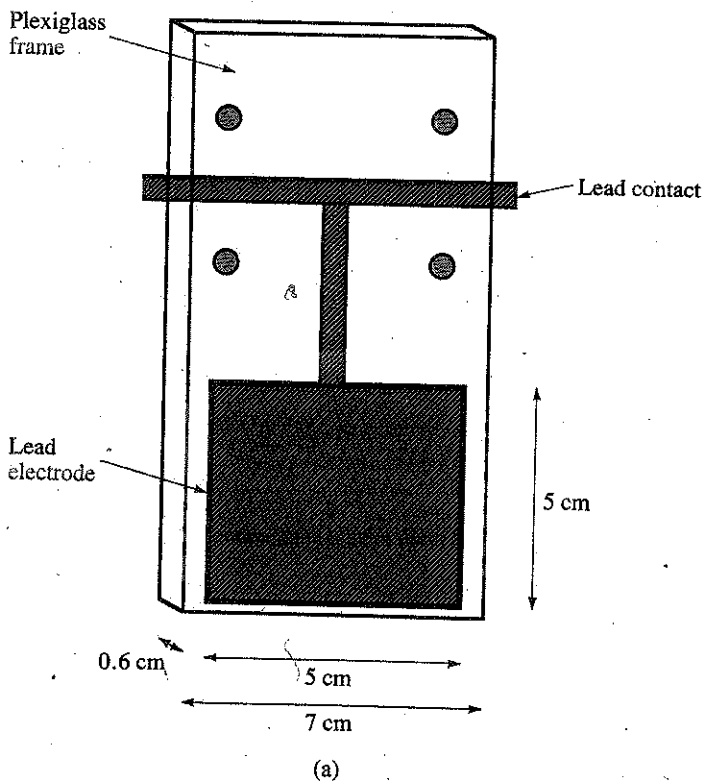
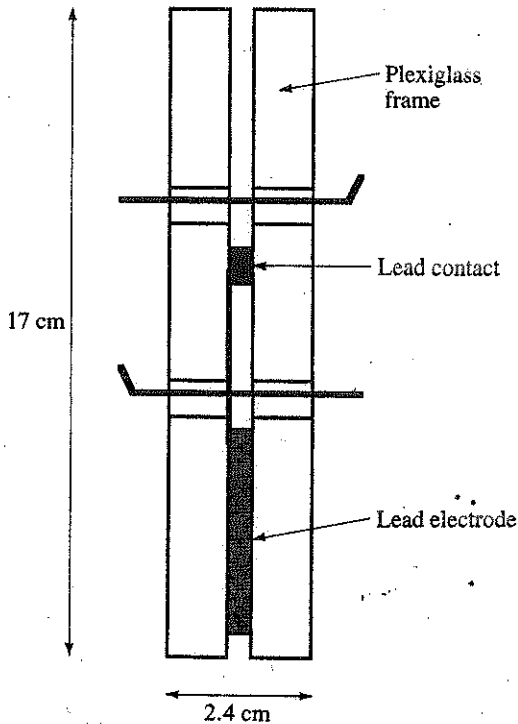


Table 29.1

Experiment type	Temperature °C	Resistance ohms	t^* hours	W^* joules
Work-producing	24	400	2.5	59
	25	200	4.0	69
	25	1,000	4.5	45
	25	2,000	6.0	40
	25	2,000	6.5	43
	42	200	0.9	185
	42	600	1.75	45
	45	2,000	3.3	25
	46	400	1.5	48
	55	3,000	1.9	11.4
Self-discharge	25	—	15.2	—
	43	—	4.3	—
	50	—	4.0	—
	55	—	2.3	—

Note: t^* = time required for the cell voltage to drop down to 3% of its final value.
 W^* = Work produced from time zero to time t^* .



(b)

equilibrium state (not a thermodynamic equilibrium state). As such, the energy transfer need not be accompanied by entropy transfer and, therefore, no entropy need be accommodated in another system, such as a low-temperature reservoir. So the process can be fast without being irreversible. In the latter case, the energy transfer out of the high-temperature reservoir is unavoidably accompanied by entropy transfer. This entropy must be accommodated in the lower-temperature reservoir, and this accommodation unavoidably requires a generation of entropy by irreversibility. Moreover, for a given temperature difference, the rate of entropy generation reduces to zero only when the rate of energy transfer approaches zero or, equivalently, the process lasts infinitely long.

Suggested headings

WP experiment: $R = \underline{\hspace{2cm}}$ ohms

Time t (minutes)	Voltage V (volts)	Current I (amperes)	Power $I \times V$ (watts)	Work $W = \int_0^t P dt$ (joules)

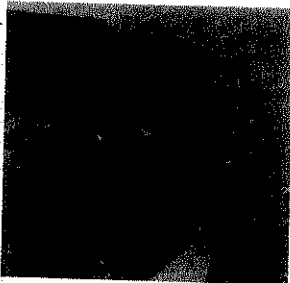
SD experiment:

Time t (minutes)	Voltage V (volts)

Reference

1. Bode, H., *Lead Acid Batteries*, Wiley, New York, 1977.

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Elias P. Gyftopoulos is Ford Professor of Mechanical Engineering and of Nuclear Engineering at the Massachusetts Institute of Technology. His book, *Thermodynamics: Foundations and Applications* (co-authored with J. P. Beretta), was published by Macmillan, New York, in 1991.

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