HOW A *CLEVER* DEMON NEARLY BLEW UP THE SECOND LAW OF THERMODYNAMICS

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The best you can do is break even.
. . . first law of thermodynamics

You can't even break even.
. . . second law of thermodynamics

Heat can not pass from a cooler body to a hotter body without some other process occurring.
. . . second law of thermodynamics

The entropy, or disorder, of the universe as a whole cannot be made to decrease.
. . . second law of thermodynamics

Is all this really true? In 1871, the Scottish physicist James Clerk Maxwell suggested that a creature small enough to see and handle individual molecules might be exempt from the second law of thermodynamics. This creature soon came to be called "Maxwell's demon" because of its far-reaching subversive effects on the nature of things.

In the years since, theorists have spent countless hours trying to save the second law. Nearly all their proposals have been flawed. Flaws often arose because the workers had been misled by advances in other fields of physics; many thought (incorrectly) that various limitations imposed by quantum theory invalidated Maxwell's demon.

The real reason why Maxwell's demon cannot violate the second law has been uncovered only recently. It is a very unexpected result of a very different line of research—research on the energy requirements of computers. It is an information-based approach which involves keeping track of the information that the devil requires, including the way it stores and erases that information.

MAXWELL'S DEMON

To quote Maxwell:[1]

> One of the best established facts in thermodynamics is that it is impossible in a system enclosed in an envelope which permits neither change of volume nor passage of heat, and in which temperature and pressure are everywhere the same, to produce any inequality of temperature or pressure without the expenditure of work. This is the second law of thermodynamics, and it is undoubtedly true as long as we can deal with bodies only in mass, and have no power of perceiving or handling the separate molecules of which they are made up. But if we can conceive a being whose faculties are so sharpened that he can follow every molecule in his course, such a being, whose attributes are still as essentially finite as our own, would be able to do what is presently impossible for us. For we have seen that molecules in a vessel full of air at uniform temperature are moving with velocities that are by no means uniform, though the mean velocity of any great number of them, arbitrarily selected, is almost exactly uniform. Now let us suppose that a vessel is divided into two portions, A and B, by a division in which there is a small hole, and that a being, who can see the individual molecules, opens and closes this hole, so as to allow only the swifter molecules to pass from A to B, and only the slower ones to pass from B to A. He will thus, without expenditure of work, raise the temperature of B and lower that of A, in a contradiction to the second law of thermodynamics.

The "being" soon came to be known as Maxwell's demon.[2-4] Such a demon, if it existed, would abolish the need for energy sources such as oil, uranium, and sunlight. Machines of all kinds could be operated without batteries, fuel tanks, or power cords.

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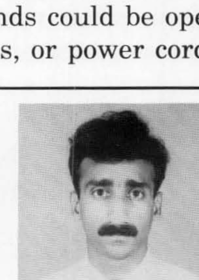

For example, the demon would be able to run a steam engine continuously, without fuel, by keeping the engine's boiler perpetually hot and its condenser perpetually cold.

Maxwell offered no definitive refutation of the demon, beyond saying that we lack its ability to see and handle individual molecules. This is not a completely satisfying exorcism of the demon because it leaves open the question of whether a being able to see and handle molecules (if such a being did exist) could violate the second law.

OTHER DEMONS

Since Maxwell's day, numerous versions of the demon have been proposed. One of the simplest creates a pressure difference (rather than a temperature difference) by allowing all molecules, fast or slow, to pass from B to A, but preventing them from passing from A to B. Eventually most of the molecules will be concentrated in A, and a partial vacuum will be created in B. This demon is, if anything, more plausible than Maxwell's original demon, since it would not need to be able to think or see.

Like Maxwell's original demon, the "pressure demon" could be a source of limitless power for machines. For example, pneumatic drills of the kind used to cut holes in the streets generally run on compressed air from a tank kept full by a gasoline powered compressor.

This demon is like a one-way valve for molecules and could be visualized as a simple inanimate device—a miniature spring-loaded trap door. Imagine that the door opens to the left. If the demon works as it is supposed to, then every time a molecule from the room on the right strikes the door, the door swings open and the molecule passes into the room on the left. When the molecule from the left strikes the door, however, the door slams shut, trapping the molecule. Eventually all the molecules are trapped on the left and the demon has compressed the gas (reducing its entropy) without doing any work.

However, this trapdoor demon is flawed. First of all, the spring holding the door shut must be rather weak. The work of opening the door against the spring's force must be comparable to the average kinetic energy of the gas molecules. In 1912, Marian Smoluchowski[5] pointed out that since the door is repeatedly struck by molecules it will eventually acquire its own kinetic energy of random motion, *i.e.,* heat energy. The door's energy of random motion will be about the same as that of the molecule striking it, and so the door will jiggle on its hinges and swing open and shut, alternately bouncing against its jamb and swinging open against the force of the spring.

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When the door is open, it obviously cannot function as a one-way valve since molecules can pass freely in both directions. One might still hope that the door would act as an inefficient demon, trapping at least a small excess of gas on the left—but it cannot do even that. Any tendency the door has to act as a one-way valve, opening to let a molecule go from right to left, is exactly counteracted by its tendency to do the reverse—to slam shut in front of a molecule that has wandered in front of it, actively pushing the molecule from the room on the left to the one on the right (aided by the force of the spring).

The two processes—a molecule pushing its way past the door from right to left, and the door pushing a molecule from left to right—are mechanical reverses of each other. In an environment at constant temperature and pressure, both processes would take place equally often, and the ability of the trapdoor to act as a one-way valve would be exactly zero. Therefore, it cannot work as a demon.

THE SZILARD ENGINE

Even though a simple mechanical demon cannot work, perhaps an intelligent one can. Indeed, some time after Maxwell had described the demon, many investigators came to believe that intelligence was a critical property that enabled the demon to operate. In a paper in 1914, Smoluchowski[6] remarked, "As far as we know today, there is no automatic, permanently effective perpetual motion machine, in spite of molecular fluctuations, but such a device might, perhaps, function regularly if it were appropriately operated by intelligent beings."

This apparent ability of intelligent beings to violate the second law called into question the accepted belief that such beings obeyed the same laws as other systems. In 1929, the physicist Leo Szilard, in his paper "On the Decrease of Entropy in a Thermodynamic System by the Intervention of Intelligent Beings,"[7] attempted to escape from this predicament by arguing that the act of measurement, by which the demon determines the molecule's speed (or, in Szilard's version of the apparatus, determines which side of the partition it is on) is necessarily accompanied by an entropy increase sufficient to compensate the entropy decrease obtained later by exploiting the result of the measurement.

Szilard considered a demon that differed in several ways from Maxwell's and it has since come to be called the Szilard engine. The engine described here is a slightly modified version by Bennet[2] of the original Szilard engine. The engine's main component is a cylinder in which there is a single molecule in random thermal motion. Each end of the cylinder is blocked by a piston, and a thin, movable partition can be inserted into the middle of the cylinder to trap the molecule in one half of the cylinder (see Figure 1).

The engine's cycle consists of six steps. In the first step the partition is inserted, trapping the molecule on one side or the other. Szilard argued that the work necessary to insert the partition can be made negligibly small.

In the next step the demon determines in which half of the apparatus the molecule has been trapped. The devil's memory has three possible states: a blank state to signify that no measurement has been made, and L to signify that the molecule has been observed in the left half of the apparatus, and an R to signify that the molecule has been observed in the right half. When the measurement is made, the memory switches from the blank state to one of the other two.

The third step, which is similar to a compression stroke, depends on the knowledge gained during the preceding step. The piston on the side that does not contain the molecule is pushed in until it touches the partition. As the piston is compressing empty space, this compression stroke requires no work. The molecule which is trapped on the other side of the partition cannot resist the piston's movement.

In the fourth step the partition is removed, allowing the molecule to collide with the piston that has just been advanced. The molecule's collision exerts a pressure on the face of the piston.

In the fifth step, which is similar to a power stroke, the pressure of the molecule drives the piston backwards to its original position, doing work on it. The energy the molecule gives to the piston is replaced by heat conducted through the cylinder walls from the environment (so the first law of thermodynamics is not violated). The molecule thus continues at the same average speed. The effect of the power stroke is therefore to convert heat from the surroundings into

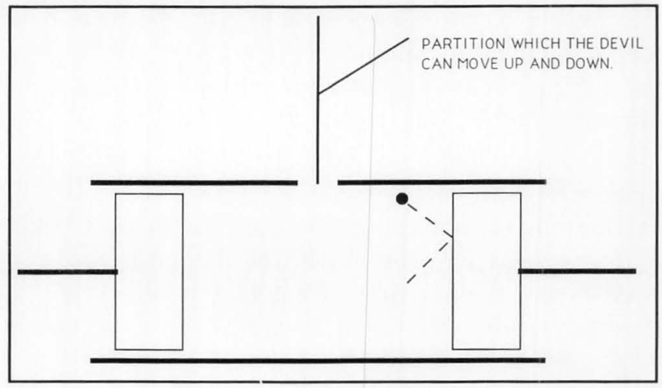

Figure 1. *The Szilard Engine*

mechanical work done on the piston.

In the sixth step the engine erases its memory, returning it to the blank state. The engine now has exactly the same configuration that it had at the beginning of the cycle.

Overall, the six steps seem to have converted heat from the surroundings into work, while returning both the gas and the engine to the same state they were in at the beginning. If no other change has occurred during the cycle of operation, the entropy of the universe as a whole has been lowered. In principle, this cycle can be repeated as often as the experimenter wants, leading to an arbitrarily large violation of the second law.

Szilard postulated that the act of measurement, in which the molecule's position is determined, brings about an increase in energy sufficient to compensate for the decrease in entropy brought about during the power stroke. Szilard was slightly vague about the nature and location of this entropy increase, but a widely held interpretation of the situation, ever since his paper appeared, has been that measurement is inevitably an irreversible process, attended by an increase in entropy of the universe as a whole by at least k ln2 per bit of information acquired by measurement.

OVERPOWERING THE DEMON

To defeat Maxwell's demon, recourse to a totally different line of approach had to be taken: the thermodynamic cost of computation in digital computers.

According to Bennet,[8] the usual digital computer performs operations that seem to throw away information about the computer's history, leaving the machine in a state where the immediate predecessor is ambiguous. Such operations include erasure or overwriting of data, and entry into a portion of the program addressed by several different transfer instructions. In other words, the typical computer is logically an irreversible or entropygenerating process and produces a great deal of waste heat, enough to require elaborate cooling strategies in some computers.

Landauer[9] showed that the fundamental source of dissipation was the erasure of information. For example, logic circuits have the property of being noninvertible, *i.e.,* from the output of a logic circuit one cannot always reconstruct the input. Landauer asserted that the logical noninvertibility translates into physical irreversibility and hence a loss of useful energy. He imagined an abstract phase space, with one coordinate being the information content of a logic device. Prior to an erasure operation, for example, the device can have two states (0 or 1). Afterward it can have only one—the standard state of an erased bit. Consequently, the extent of occupied space in the logical coordinate is reduced by two, and the occupied volume must expand in the other coordinates. These coordinates represent things like thermal vibrations in whatever physical system the logic device is implemented. Excitation of thermal vibrations means heat is generated.

According to Zurek,[10] reversible computation can be accomplished only by using computer memory to keep track of the exact path from the input to the output. This is based on the observation that thermodynamic irreversibility is inevitable only in the presence of logically irreversible operations. If several input states lead to the same output, the loss of information in such a many-to-one mapping makes it impossible to reversibly "backtrack" the machinery of the computer. To allow reversible operation the computer must retain this additional information (*i.e.,* the history of all logically irreversible steps) at least temporarily, and it must retain at the end of the computation at least enough information to assure unambiguous backtracking. Thus, reversible computation can be achieved only at the expense of filling up computer memory with historical records, aptly named "garbage."

Now, consider the operating cycle of Szilard's engine. The last step in which the engine's memory is reset to a blank state is logically irreversible because it compresses two states of the machine's memory ("the molecule is on the left" and "the molecule is on the right") into one ("the molecule's position has yet not been measured"). The demon cannot reset its memory without adding a bit to the environment.

Landauer[11] has shown that the energy needed to erase a bit is precisely kT ln2. This converts all the work that had been gained during the power stroke to heat. So the demon cannot violate the second law because it must forget the results of the earlier observations in order to observe a molecule.

Consider a case where the demon has a very large memory and simply remembers the results of all its measurements. There would be no logically irreversible step, and the engine would convert one bit's worth of heat into work—seemingly jeopardizing the second law. The point to note here is that the cycle is not a true cycle. Every time around, the demon's memory, initially blank, would acquire another random bit. The correct thermodynamic interpretation of the situation would be to say that the demon increases the entropy of its memory in order to decrease the entropy of its environment. Here useless information about the outcomes of past measurements piles up. The process uses the devil's memory as a zero-entropy reservoir. To make the process truly cyclic, the memory has to be periodically erased, and the cost of erasure must be subtracted to calculate the actual amount of useful work extracted.

Caves[12] suggests that a Maxwell demon may be able to extract work by waiting for rare thermal fluctuations. His system consists of a number of Szilard engines coupled together. The trick lies in briefing the demon, which must be told to extract work from the engine only when the storage of information can be handled economically. In the extreme case, for example, the demon might be told to not extract work except when the N molecules in the N containers are on the left-hand side of their respective partitions. Then, the work the demon can arrange to be produced is NkT ln2. The state can be represented by only a single bit, the erasure of which will require only the expenditure of kT ln2.

This led Caves to conclude that Maxwell's demon could indeed extract work by waiting for thermodynamic fluctuations that are, by definition, rare. Thus it would appear that the second law has a modest loophole. This result (that the demon could win occasionally) was disproved before Caves' paper appeared in print.

The trouble was that the demon had to carry additional bits of memory to show whether or not it decided to use a particular configuration. Otherwise it could get caught in a loop: looking at a set of boxes, rejecting that configuration, storing no information, then not knowing whether it had checked that configuration, looking at it again, and so on. To avoid getting caught in such a loop, the demon ends up with a memory filled with a string of essentially random digits distinguishing between the useful arrangements and the rejected arrangements. There is no compact form of expressing this information.

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use and emissions than the manufacture of a paper or plastic sack, the consumer must use the sack at least ten to twenty times before an environmental benefit is achieved.

CONCLUSION

Assessing the total environmental impact of any product is a difficult process, involving evaluations of processing steps ranging from raw material acquisition to post-consumer waste disposal. Comparing the environmental impact of competing products is even more complex. Making comparisons between products usually involves making trade-offs between very different environmental impacts.

The purpose of this problem is to illustrate the difficulties involved in comparing the total environmental impact of different products. Paper and plastic grocery sacks were used as a case study. To compare paper and plastic grocery sacks we found that we must evaluate the trade-offs between energy use, pollutant emissions, and the depletion of natural resources. Plastic sacks appear to result in less atmospheric emissions and require less energy. On the other hand, paper sacks rely on a renewable resource for material and energy. Thus there is no clear, environmentally superior product. The consumer is left with a difficult choice, and as illustrated in the problem this choice must be made with incomplete information.

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Suggestions for Further Reading

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Second Law of Thermodynamics

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The extra cost of erasing these digits exactly cancels any energy gain elsewhere in the system.

The conundrum of Maxwell's demon has been resolved by applying the concepts of thermodynamics of irreversible computation.

In our discussions, we assumed the behavior of the demon to be completely deterministic, *i.e.,* one instruction is completed before it goes on to the next instruction. What is not so clear is what would happen if the demon could wander a little, *i.e.,* if the demon knew its instructions but was not quite sure of the order in which to carry them out. The demon would then proceed from one step to another, going forward or backward, in a somewhat random fashion. In the long run, this might allow the demon to extract some work.

There is no doubt what the outcome of the above argument is going to be, but it is a loophole which has yet to be closed.

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Liquid-Liquid Processes

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information is obtained by the Stirred Transfer Reactor, which is a modified Lewis cell. The interfacial area between the contacted liquid phases needed for the estimation of mass transfer and reaction rates is calculated from information about the drop size distribution and the dispersed-phase volume fraction. The former is obtained by the Microphotographic Technique and/or the Laser Capillary Spectrophotometer Technique and the latter by the Ultrasonic Technique.

Tracer concentration measurements by the Laser Photometric Technique yield information about flow properties, *i.e.,* axial mixing parameters in both phases. Drop size-concentration bivariate distributions are obtained by the Laser Capillary Spectrophotometry Technique. This information is extremely valuable in model discrimination and parameter estimation of models describing droplet breakage and coalescence. It also provides information on dispersed phase mixing. Finally, the Ultrasonic Technique is also employed for the control of the dispersed-phase volume fraction in extraction columns to secure non-flooding optimum operation.

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