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Links and lies

In which we explore connections between entropy production and exergy consumption, between free energy and exergy—and between helpful and misleading books.

You'll have guessed that entropy production and exergy consumption are linked. They are. And the linkage is encapsulated by the simple relationship: *exergy destruction equals entropy production multiplied by the environmental temperature*. With this relationship for *how* they're linked we have a great weapon for judging what's causing problems and how to better design technologies. We'll use this weapon in the next three articles of this series: "What Should We Blame?" [1] "The Skinny On efficiency" [2] and "What Will We Gain?" [3].

While the relationship is simple, understanding *how to find* the relationship is not so simple. To understand that, we need to think our way through a few other relationships that, when expressed as equations, are awkward fellows. For those readers who want to have some idea how we got the entropy–exergy connection, I'll summarize the logic over the next few paragraphs—but I'll need to use a few equations. For those who don't care—or are willing to trust—it should be comforting to know that, this little equation-squall will be brief, like most squalls. And, as before when we encountered the squally patches of our odyssey, you can go below for something hot.

The clear-cut relation between entropy production and exergy destruction is encapsulated by the equation

$$\dot{I} = T_o\dot{\Pi}, \tag{1}$$

where $\dot{I}$ is the *rate* of exergy consumption rate, $\dot{\Pi}$ is the entropy production rate and, as before, T_o is the environmental temperature. (Exergy consumption is sometimes taken to be a measure of "irreversibility", which is why it's been assigned the symbol I.) If we want exergy consumption given in terms of entropy production, we can tip over Eq. (1) so it becomes,

$$\dot{\Pi} = \dot{I}/T_o \tag{2}$$

giving entropy production as equal to exergy consumption *divided by* the environmental temperature.

These two simple relations are extraordinarily useful—far out of proportion to their simplicity (as is often the case with simple, profound equations, like, for example, $F = ma$). Sometimes it's much easier to estimate entropy production than exergy destruction, when we can use Eq. (1) to calculate exergy destruction from entropy production. Sometimes it's the opposite, when we can use Eq. (2) to calculate entropy production from exergy destruction.

As neat and tidy as the relationship between entropy production and exergy destruction appears, to *use* the relationship we must make choices.

The first choice is whether to think in terms of continuous flows (like the continuous entropy and exergy flows, to and from Earth) or in terms of lump quantities (like the entropy your car produces taking you from home to work). Most applications involve continuous flows, so Eqs. (1) and (2) are written as *rate* equations. The "dots" over the symbols I and Π mean time derivatives of those quantities—in this case the "rate" of production or destruction. If, instead, we want to write the equations for absolute quantities we'd simply remove the "dots".

The second choice is subtler. It evolves deciding what value to use for environmental temperature. This is a matter of choice, a matter of *how* we want to look at *what* we are looking at. In turn, this choice shapes how the result should be interpreted. This need for choice illustrates one of the differences between pure science, which must strive to avoid human value judgements, and engineering, which must often include value judgements or, sometimes, make terrible mistakes.

For those interested in knowing something about the mathematical jiggling and wiggling that led to Eq. (1), here is a brief outline.

The energy *rate* equation can be written as

$$\frac{dE}{dt} = \sum_i \dot{Q}_i + \sum_j \dot{W}_j + \sum_k \dot{m}_k(h_k + ke_k + pe_k + \cdots). \tag{3}$$

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The term on the left represents the rate at which energy is changing within the system—whether the system is a steam turbine, the world, or you. On the right, in sequence, we have all the ways energy can enter or leave the system—starting with heat, Q, then work, W, and finally by material, m. The symbols $\sum_{i,j,k}$ means "summed" over an arbitrary number of entry and exit locations i, j, k. The energy carried by material includes enthalpy [1], h, kinetic and potential energies … and so on. [2]

In a similar fashion, the entropy rate equation can be written as

$$\frac{\mathrm{d}S}{\mathrm{d}t} = \sum_i \frac{\dot{Q}_i}{T_i} + \sum_k \dot{m}_k s_k + \dot{\Pi}. \tag{4}$$

This time the term on the left is the rate entropy changes within the system. The terms on the right represent, in sequence, the rate heat conducts [3] entropy to and from the system, the rate material carries it in or out and, finally, the rate entropy is *produced* within the system, $\dot{\Pi}$. You'll remember that work transport doesn't involve entropy transport, [4] which is why (unlike the energy equation) there isn't a term in this entropy equation that corresponds to work.

To squeeze Eqs. (3) and (4) together, we must first multiply Eq. (4) by the environmental temperature (in part, to get the units right), add the result to Eq. (3), perform the jiggling and wiggling, and out pops the exergy rate equation

$$\frac{\mathrm{d}\Xi}{\mathrm{d}t} = \sum_i \left(1 - \frac{T_\mathrm{o}}{T_i}\right) \dot{Q}_i + \sum_j \left(\dot{W}_j - p_\mathrm{o}\frac{\mathrm{d}V}{\mathrm{d}t}\right) + \sum_k \dot{m}_k \xi_k^f + T_\mathrm{o}\dot{\Pi}. \tag{5}$$

Exergy is given the symbol Ξ. As you will expect from the way the earlier equations were set up, the term on the left is the rate at which exergy stored within the system is changing. The terms on the right follow the same sequence as earlier; the first gives the rate exergy is carried in/out by heat, the second by work (less any work the system does on the environment *if the system volume changes*), and the third by material. [5] Now we come to the last term, $T_\mathrm{o}\dot{\Pi}$. By straightforward physical interpretation of every *other* term in the equation, this must be the *rate* exergy is *destroyed* within the system. So now we know where Eq. (1) came from.

While messing about with equations, we should take one more step. The expression for exergy can be written as

$$\Xi = (E - U_\mathrm{o}) + p_\mathrm{o}(V - V_\mathrm{o}) - T_\mathrm{o}(S - S_\mathrm{o}) + \text{chemical exergy terms}. \tag{6}$$

The symbol U represents internal energy and V represents volume. We recognize S and p as entropy and pressure. The symbol E means *all* forms of energy that might be stored within the exergy-containing media—not just internal energy, but also kinetic, chemical, potential and so on. As before, the subscript "$_\mathrm{o}$" identifies properties of the exergy-containing medium *after* it's been brought into environmental equilibrium. Quantities without subscripts are properties of the exergy-containing medium when it's in some an arbitrary state, normally when it's not in environmental equilibrium.

Because we know exergy is a property of *both* the exergy-containing medium and its environment, it should not be surprising that each term on the right-hand side includes properties of *both* the medium and the environment. Moreover, it's easy to see that when the system reaches environmental equilibrium each term on the right-hand side becomes zero, making the exergy zero—as, of course, it must be. (I always feel a glow of satisfaction when equations produce what you know they must produce at key points within their range of application.)

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[1] Enthalpy is just the everyday "internal energy" we discussed earlier of a container, *plus* a term that accounts for "flow work"—the energy required to push the material in or out.

[2] When relevant, chemical energy must also be included. I've neglected it to keep things simple, because it doesn't influence the form of our conclusions.

[3] I've used the verb "conducts" because, strictly speaking, this term will be modified by a coefficient when it accounts for heat transfer by radiation. This was discussed in the 17th article of this series "The Trouble with *Micro*states". But coefficients don't help understanding, so I'm staying with the simpler—and more conventional—expressions.

[4] Indeed, work is sometimes defined as energy transport without entropy transport. This was discussed in the "The Trouble with *Micro*states".

[5] This includes a quantity called flow exergy, which is analogous to enthalpy used in the energy equation.

While we're tidying up mathematical details, I should clarify a sometimes-misunderstood connection between exergy and (what thermodynamicists call) "free energy". Free energy (usually defined in terms of Gibbs or Helmholtz functions) is a cousin to exergy, but not its equivalent. Perhaps the sharpest difference is that free energies are properties of the medium *only*. In contrast, exergy is always a property of *both* the medium *and* its environment. The confusion between the two probably exists because, under very special circumstances, the mathematical expressions for "free energy" and "exergy" appear similar—although a close look shows they're different beasts.

Nevertheless, Gibbs function is often used to calculate the "species" component of chemical exergy but not the "concentration" component—and certainly not the thermomechanical component.

Exergy and free energy may be cousins, but *not* identical twins.

Now that we've emerged from this little equation-squall, let's move on to discuss connections between entropy, exergy and some well-known and less well-known books.

Several years back, while putting-in-time at one of the worst putting-in-time places in our modern world, I found the airport bookstore. There I stumbled on *Entropy* by Rifkin [4]. Great! This would be fun. Perhaps it would give me ideas I could use in my introductory thermodynamics course. I began reading even before boarding the airplane. But soon I knew reading through to the end would be painful. We hadn't pushed back from the ramp when, metaphorically, I was reaching for the airsick bag.

Entropy is an attempt by a popular writer to use selected, misinterpreted ideas from entropy theory to tell us, once again, that we're all going to hell in a hand basket. Here was an emotional, populist conclusion marching resolutely backwards in search of supporting scientific principles. Except Rifkin got it all wrong. Was this a masterpiece of scientific misunderstanding or purposeful misleading? I felt a mixture of anger and sadness. I consider entropy concepts to be one of the most important yet least understood aspects of designing modern energy systems. Its significance for life is intriguing but it hasn't, so far, attained the practical significance that it has for our energy technologies. Yet here was Jeremy Rifkin blatantly misleading readers about our civilization and the future of our planet.

In *Full House*, Stephen Jay Gould [5] tells us that M. Scott Peck's *The Road Less Traveled*, first published in 1978, has placed itself so far ahead in total sales that there can be no challenge. Yet, as Gould points out, in his chapter "The Miracle of Evolution", [6] Peck reinforces the continuing misunderstanding of the entropy law, by writing:

> "*The most striking feature of the process of physical evolution is that it is a miracle. Given what we understand of the universe, evolution should not occur, the phenomenon should not exist at all. One of the basic natural laws is the second law of thermodynamics, which states that energy naturally flows from a state of greater organization to a state of lesser organization …. In other words, the universe is in a process of winding down*". Peck, in effect, claims evolution is miraculous because it violates the second law, "… since, as a process of increasing organization and differentiation, it runs counter to natural law". Worse, Peck says life must be an "… *evolutionary force that has so successfully and consistently defied* "*natural law*" *over millions upon millions of generations that it must itself represent a natural law as yet undefined*".

In spite of publication after publication that "gets it wrong" there are many books that "get it right". Of these, *Full House* just quoted is one—and it's about life sciences. James Lovelock, who wrote about life in *The Ages of Gaia* says:

> "*There are three equally powerful approaches* (in our quest to understand life): *molecular biology, the understanding of those information-processing chemicals that are the genetic basis of all life on Earth*; *physiology, the science concerned with living systems seen holistically*; *thermodynamics, the branch of physics that deals with time and energy and that connects living processes to the fundamental laws of the Universe. Of these sciences, the latter is the one that may go the furthest in the quest to define life, yet so far has made the least progress. Thermodynamics grew from down-to-earth origins, the quest of engineers to make steam engines more efficient*". Lovelock then goes on to write: "*Entropy is real, not some hazy notion invented by professors to make it easier to challenge students with difficult examination questions*". And then: "*The second law is the most fundamental and unchallenged law of the Universe*; *not surprisingly, no attempt to understand life can ignore it*".

I've quoted Peck and Lovelock at length because the first is an honest statement by, I presume, a sincere, honest man that shows how pervasive the misunderstanding of entropy is, while the second is by an eclectic scientist who not only fully understands the second law of thermodynamics, but (I think with great prescience) anticipates the significance entropy analysis may come to have in our future understanding of living systems. I see nothing redeeming in Rifkin's nonsense. [6]

[6] I believe Rifkin has lost all credibility among responsible scientists. Stephen J. Gould gave a scathing dissection of Rifkin's pretentiousness and incompetence in "Integrity and Mr. Rifkin". The wonderful book, *Higher Superstition* by Paul R. Gross and Norman Leavitt gives an entertaining, yet frightening, examination Rifkin's irresponsible rhetoric—as one example of carcinogens to public understanding.

In an earlier article, I recommended a second book authored by Lynn Margulis and Dorion Sagan, and using the same title as Schrödinger's *What is Life*? [7]. Written by two first-rate life scientists and founded on the thermodynamic fundamentals set out by Schrödinger, this is truly a wonderful book. The graphics are exquisite and the explanations mesmerizing.

This is the twenty-first in a series of articles

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