AC 2007-223: ESCAPE FROM CARNOT: A NEW WAY TO INTRODUCE THE MYSTERIOUS PROPERTY, ENTROPY.

Andrew Foley, U.S. Coast Guard Academy

Escape from Carnot :
A new way to introduce the mysterious property, Entropy.

Dr Andrew C Foley P.E
U.S Coast Guard Academy,
New London, CT

Introduction

Entropy and its use within the second law of thermodynamics is undoubtedly one of the harder concepts in an undergraduate engineering degree. The vast majority of engineers fall into one of two categories when use of the second law is discussed. The first are those that can effectively get by without the second law, able to solve most problems with careful use of the first law. The second category are those that use the second law correctly but simply as a tool without an in depth physical understanding. This is not uncommon in engineering as one simply has to think of the widespread use of Laplace transforms, or more recently the surge in the use of complex stress analysis or computational fluids software where users do not understand the intricacies of the tool but use them anyway. While not ideal this approach is invariably successful as long as the limitations of the tool are not exceeded. Comfort is gained in the knowledge that numerous previous users have successfully used the same tools and hence undertaken a type of ‘validation by the masses’. If in doubt about these assertions the author challenges the reader to ask several engineers/academics to briefly describe the physical nature of entropy.

To further elaborate on the issue of understanding entropy one only needs examine several core thermodynamic texts. (e.g Cengel & Boles (2006), Rogers & Mayhew (1980)) The second law is invariably introduced by using abstract heat engines and assorted assumptions, which eventually allow an expression for the property entropy, as heat flux over temperature to be derived. This can add to confusion as heat flux itself is not a property but rather energy in motion. Also the idea of energy exchanges between at least two reservoirs always being necessary and then the actual Kelvin-Planck statement of the Second Law itself only add to the confusion. i.e. ‘It is impossible for any device to exchange heat from a single reservoir and produce a net amount of work’. Even after one goes through the classical build up to the above statement, attentive students will still ask “how does that statement come from that example?”. As an instructor who has successfully brought his class to relative mastery of the first law, it always proves disheartening to suddenly see a class start to flounder with the second law.

Klotz(1964) alludes to this difficulty with the statement “ the heart of the difficulty in understanding the concept of increase in entropy is a verbal one “ He goes on to state “ one should realize that entropy is essentially a mathematical function”. So promoting the “simply use it as a tool” approach used by the second type of user described in the opening paragraph..

Recognizing the conceptual difficulties while still holding out for a physical understanding of entropy this paper describes a method of bringing the second law ‘on line’ in a consistent manner with how the first law is already being taught. (Foley

(2005)). In doing so it is found that students are more accepting of the law and generally more comfortable in describing what entropy is.

Reynolds Transport Equation : the first law and then the second law as more of the same.

In a previous paper Foley (2005) describes a method of introducing the first law using the Reynolds Transport equation. Briefly a generic property B is considered with respect to a general ‘catch all’ control volume. (See Figure 1.)

$$\frac{DB}{Dt} = \frac{\partial B}{\partial t} + \sum \dot{B}_{net_gen} + \sum (\dot{mb})_{net_in} \quad \dots\dots(1)$$

Note that the summation signs have been used instead of the integral sign to reflect that most of the problems in an introduction to thermodynamics course involve discrete inputs, outputs etc. While not to the ‘purists’ satisfaction it has worked well with students who later ‘ramp up’ to functional, continuous type inputs with little difficulty.

Using equation (1) the property B can then be replaced with energy in its various guises and the accounting of energy through the control volume becomes :

$$\frac{DU_{CV}}{Dt} = \frac{\partial U_{int\,ernal}}{\partial t} + \sum \dot{Q}_{net_in} - \sum \dot{W}_{net_out} + \sum (\dot{me})_{net_in} \quad \dots\dots(2)$$

By treating the surroundings (i.e. Everything else) as just another control volume one can apply the same accounting exercise to the surroundings:

$$\frac{DU_{SUR}}{Dt} = \frac{\partial U_{int\,ernal}}{\partial t} + \sum \dot{Q}_{net_in} - \sum \dot{W}_{net_out} + \sum (\dot{me})_{net_in} \quad \dots\dots(3)$$

Finally, by adding the two rates of change, equation (2) and (3), it was hypothesized by Joule and Clausius that, in the absence of Nuclear reactions, the sum should always equal zero. That is, the energy is conserved. i.e.

$$\frac{DU_{SUR}}{Dt} + \frac{DU_{CV}}{Dt} = 0 \quad \dots\dots(4)$$

This hypothesis became so established that, in the absence of any formal proof, it was eventually elevated to the status of a law, the first law of thermodynamics. Energy will always be conserved.

So much for the first law, to introduce the second law in this form the idea of energy reversibility first needs to be broached. Some examples are used to elucidate the idea.

In figure 2 one can see that the kinetic energy (K.E) of the skate boarder is transferred into potential energy (P.E) as she moves up and down the half pipe. In reality some of the energy is 'degraded', as it is converted by friction into heat. However, to a reasonable approximation one can picture that for each traverse of the pipe most of the energy transfer is recoverable or, as is more commonly stated in thermodynamics texts, the energy is reversible between the kinetic energy of motion and the potential energy of the skateboarder relative to the ground. Because of this reversibility 'quality' degradation of that energy has not occurred.

Similarly kinetic energy of air in a multi-stage aircraft compressor is continually diffused in order to increase pressure-volume energy. This stored 'pressure energy' could quickly be transferred back to Kinetic energy and so be effectively reversible. Some fraction of the energy, however is invariably transferred via friction and hence heat flow into the internal energy of the air. This internal energy manifests itself as an increase in temperature and cannot then be transferred back into kinetic energy. The term 'cannot' is used because nobody has, as yet, been able to do this. Indeed such is our confidence in this belief/hypothesis that it too has taken on the form of a thermodynamic law, the second law. This lack of reversibility in all physical processes has tremendous implications to mankind. While energy is re-assuredly conserved it is none the less being continually degraded. As its usefulness to mankind is not only measured by the quantity but also the 'quality' of the energy this perpetual degrading means that our ability to use energy is also being continually reduced.

Returning to the purpose of this paper we can now surmise that it would be very useful if, as we undertook our energy transfers, we could use a gage to quantify the degradation of energy 'quality' through our various processes or systems. A rapidly rising entropy reading would alert us to areas of high energy degradation and also allow us to compare different processes more appropriately.

Entropy.

It turns out that there exists a property called Entropy which can be used as an indicator of how the quality of energy is being degraded. This is the property our imaginary gage must measure.

Just like our first law equation this property can be placed into the Reynolds Transport Equation :

$$\frac{DS}{Dt} = \frac{\partial S}{\partial t} + \sum \dot{S}_{net_direct} + \sum (\dot{m}s)_{net_in} \quad \dots\dots\dots(5)$$

Entropy accumulating in the control volume

Entropy spontaneously generated within the control volume

Entropy transferred directly into/out of the control volume

Net Entropy convected in with mass flow

After beginning this explanation with a simple acknowledgment that this ‘property’ exists as a means to measure energy quality degradation it is now imperative to illustrate how it can be physically interpreted.

Entropy out of the first law

Using examples other than the traditional Carnot Engine was a goal of this method of instruction. Note however that the Carnot Cycle efficiency derivation is still undertaken later in the course and becomes a relatively trivial exercise.

Example 1. The internal entropy generation and convected entropy terms found using an orifice plate

Figure 3 shows a simple orifice plate arrangement with air flowing along the pipe. Starting with the first law it can easily be shown:

$$e_{in} - e_{out} = 0 \quad \text{or more compactly} \quad de = 0$$

Now the specific energy of flowing fluid in this case comprises the following terms:

$$e = u + pv + gh + \frac{V^2}{2} \quad \dots\dots\dots(6)$$

(N.B Other forms of energy storage such as magnetic, electric, chemical etc. could be included if required).

Hence for our orifice plate control volume

$$de = \underbrace{du + pdv}_A + \underbrace{vdp + gdh + VdV}_B = 0 \quad \dots\dots\dots(7)$$

Examining the terms in the A circle first i.e. $du + pdv$

By inspection both of these terms relate to energy changes that are irreversible. The first term represents an increase in internal energy of the air. This energy cannot be reversed out of the air and turned back into kinetic energy. (e.g. When water is warmed up, it will not spontaneously cool down and return that energy to whence it came). Similarly the second term relates to an expansion, and an expanded gas, fluid or solid will not spontaneously re-compress itself. This energy therefore, cannot be recovered after it has been diffused and hence degraded.

As for the three other B terms in the equation, $vdp + gdh + VdV$

The first term corresponds to increasing the pressure in a fixed volume, this is akin to compressing a spring and hence it is intuitive that this compressed energy can be reversed into potential energy, kinetic energy or used directly to do work.

The final two terms are also seen to be reversible, the skateboarder in the half pipe illustrated how these two can be reversed into each other.

What we want from our ‘quality’ gage therefore is an indication not of the total quantity of energy but instead the increase in the ‘unrecoverable’ or ‘bad’ energy i.e. the A terms.

$$de_{bad} = du + pdv \quad \dots\dots\dots(8)$$

Which for the air in our pipe can be simplified to :

$$de_{bad} = C_v dT + pdv \quad \rightarrow \quad de_{bad} = C_v dT + \frac{RT}{v} dv \quad \dots\dots\dots(9)$$

If temperature, T was a constant, i.e. in an isothermal processes, we could integrate equation (9) and quantify the energy degraded. Arguably that would ultimately be the end of the story. Unfortunately temperature in most cases is not so obliging and hence in order to be able to progress equation (9) to some sort of ‘solution’ we could make a division by T, such that :

$$\frac{de}{T}_{bad} = \frac{C_v}{T} dT + \frac{R}{v} dv \quad \dots\dots\dots(10)$$

By undertaking this mathematical convenience we are now able to integrate the right hand side. i.e.

$$\int \frac{de_{bad}}{T} = C_v \ln \frac{T_2}{T_1} + R \ln \frac{v_2}{v_1} \quad \dots\dots\dots(11)$$

Unfortunately what we derive on the right hand side is not now the quantity of energy degraded, instead it is the next best thing, ***a property that acts as a gage as to how much degradation has occurred.*** If our right hand integral evaluates to zero then we have the best process possible. There has been no degradation. Anything else and we have had a reduction in the quality of the energy.

The term $\int \frac{de_{bad}}{T}$ is the increase in Entropy and is given the symbol S.

This is different from most text book definitions which normally give entropy as : $\int \frac{Q}{T}$

This is normally a result of its derivation from a Carnot engine type problem where heat transfer is the primary source of energy degradation. I believe the format presented in this paper is more helpful in that all forms of energy degradation can be wrapped up into the energy degradation term. Energy is also a property and as such, its use rather than Q , which is an energy in transition term, is intuitively more helpful.

It is worth mentioning that just because entropy cannot be directly measured, but instead must be derived from other thermodynamic properties, one should not be too disheartened. Most properties are indirectly measured. E.g. the measurement of temperature by mercury expansion or mass by weight measurement.

So, finally examining our second law for the control volume surrounding the orifice plate in the pipe we get :

$$\frac{DS}{Dt} = \frac{\partial S}{\partial t} + \sum \dot{S}_{net_direct} + \sum (\dot{m}s)_{net_in}$$

Which for steady state conditions reduces to

$$\frac{\partial S}{\partial t} = -\sum (\dot{m}s)_{net_in} = \dot{m} \left[C_p \ln \left(\frac{T_2}{T_1} \right) + R \ln \left(\frac{P_2}{P_1} \right) \right]$$

i.e. The entropy generation term and its resultant convected terms can be calculated for a gas from a knowledge of its start and end pressure and temperatures.

Example 2 The direct heat transfer Entropy creation term. Introduced via cooling of a volume of warm air released into the atmosphere.

Figure 4 shows a volume of warm air suddenly released into the atmosphere

Here the first law for the warm air control volume and the surroundings air reduces to

$$DU_{CV} + DU_{SUR} = Q_{out} - Q_{in} = 0 \quad \dots\dots\dots(12)$$

In this case all the heat transfer Q has been dispersed from the higher temperature air to the lower temperature atmosphere and is now unrecoverable. i.e. Our entropy gage would show an increase in entropy relating to this energy degradation.

Using our ‘trick’ from example 1 we know that the entropy is the increase in ‘bad’ energy divided by temperature. So in this case, (assuming for the purposes of illustration, constant temperature of the warm air and the surroundings),

$$DS_{total} = \frac{DU_{SUR}}{T_{SUR}} + \frac{DU_{CV}}{T_{CV}} = \frac{Q}{T_{SUR}} + \left(\frac{-Q}{T_{CV}} \right) \dots\dots\dots(13)$$

which because the surroundings are at a lower temperature will mean that, as expected, the total Entropy will increase.

Therefore for our individual entropy accounting equations, with a variable temperature, it is consistent to use $\delta S = \int \frac{Q}{T}$ as the term showing entropy transfers due to direct heat transfer.

First law ‘morphs’ into the second law

Neglecting any work terms in our first law, which by definition are completely reversible our second law can be ‘morphed’ from the first law as follows :

$$\begin{aligned} \frac{DU_{CV}}{Dt} &= \frac{\partial U_{internal}}{\partial t} + \sum \dot{Q}_{net_in} - \sum \dot{W}_{net_out} + \sum (\dot{m}e)_{net_in} \\ \downarrow \quad \quad \downarrow \quad \quad \downarrow \quad \quad \quad \downarrow \\ \frac{DS_{CV}}{Dt} &= \frac{\partial S_{internal}}{\partial t} + \sum \frac{\dot{Q}}{T_{net_in}} + \sum (\dot{m}s)_{net_in} \dots\dots\dots(14) \end{aligned}$$

Finally if one then adds the entropy accounting equation for both system and surroundings we can then write the second law of thermodynamics :

$$\frac{DS_{SUR}}{Dt} + \frac{DS_{CV}}{Dt} \geq 0 \dots\dots\dots(15)$$

Note most importantly, the lack of an equal sign. Again this originated as a hypothesis based on multiple observations that energy is invariably degraded in its usefulness or ability to be reversed. Because of this spontaneous degradation entropy can effectively be generated out of nothing ! With the generation of nuclear energy the same issue could be said to apply to the energy equation. This is resolved however when the equivalence between mass and energy is realized. No such resolution has yet been determined for the second law and hence the inequality remains.

Finally, this hypothesis, as with the first law, has over time built up its status eventually justifying its promotion to, ‘The Second Law of Thermodynamics’.

Conclusions

The Reynolds Transport Equation as a means of accounting for properties was first introduced. This equation is applied to a system and its surroundings and an assumption of conservation is made. The result of this is then given as the first law of thermodynamics. The author has used these tools relatively painlessly in getting students very proficient in solving the majority of the thermodynamic problems they will encounter as practicing engineers. (i.e. First law applications.) The challenge detailed in this paper was to use some simple examples as well as the same basic tools used for the first law to introduce the property entropy and then ultimately the second law of thermodynamics. By being consistent with the first law principles and equation formats the author believes he has kept students more in contact with the instruction and ultimately more comfortable with using entropy as a gauge for energy degradation. Interestingly after the completion of this process the derivation of a maximum heat engine Carnot efficiency was undertaken as a class example without any particular complications.

References

- A.C.Foley (2006)*** Applying the ‘catch all’ general control volume and the Reynolds transport equation to improve thermodynamic instruction.. ASEE National Convention, Chicago 2006.
- Kotz, I.M. (1964).*** Chemical thermodynamics, basic theory and methods. W.A.Benjamin,inc, New York. (pp.129)
- Rogers G.F.C. and Mayhew Y.R. (1983).*** Engineering Thermodynamics, Work and Heat Transfer, 3rd Edition. Longman Group Ltd., New York
- Cengel Y.A. & Boles M.A. (2006).*** Thermodynamics, an engineering approach. 5th Edition.McGraw Hill, New York.

Figure 1. The general Control Volume for Accounting for property B

Figure 2. The reversibility of K.E and P.E types of Energy.

Figure 3. The orifice plate used to introduce the concept of entropy without external heat transfer.

Figure 4. Entropy production due to heat transfer alone.