

## SECOND LAW CONCEPTS

### 4. Topic: Entropy

#### **Engage:**

Take a pack of children's balloons into class. Hand one to each student. Ask the students to blow up their balloons and place them in a tidy pile in a corner of the room.

Of course you will not end up with a tidy pile! Unless you have a little static electricity around as in the photograph.



#### **Explore:**

Ask the students what they feel when they gather round a barbeque on a late Fall day, or when they light the gas on the stove on a cold day. The answer should be heat! Ask them to discuss in pairs how the pile of balloons is analogous to heat from the gas stove or barbeque. Invite a couple of pairs to offer their explanation.

The balloons have a tendency to disperse; it is impossible to make a pile of them unless we use a box or a net to constrain them. Energy behaves in same way. Energy will always disperse unless it is constrained from doing so. Our most common experience of this dispersion is heat transfer as in the case of the gas stove or barbeque. The measure of energy dispersion is entropy.

#### **Explain:**

Rudolf Clausius expressed his statement<sup>Ⓢ</sup> of the second law of thermodynamics as

$$\oint \frac{\delta Q}{T} \leq 0$$

where  $\oint$  means the integral or sum around a cycle, and  $\delta Q$  is the heat entering the system at a point in the cycle and at temperature T.

Clausius called the quantity on the left of the above equation 'entropy', which is denoted by S and

$$dS = \frac{\delta Q}{T} \text{ so } \oint dS \leq 0$$

For a reversible process the equality applies, but for all other processes more entropy is transferred out of the system than into it.

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<sup>Ⓢ</sup> It is impossible for any system to operate in thermodynamic cycle and produce no effect other than the transfer by heat from a cooler to a hotter body.

The third law of thermodynamics defines the absolute value of entropy: *the entropy of a pure crystalline substance at absolute zero temperature is zero*. For a pure crystalline substance at absolute zero temperature we have no uncertainty about the state of its molecules which leads to a second definition of entropy based on statistical mechanics

$$S = k \times \ln W$$

where  $W$  is number of microstates that are consistent with the given macrostate and  $k$  ( $=1.380658 \times 10^{-23}$ ) is the Boltzmann constant (named after Ludwig Boltzmann who proposed the above relationship) and is the ratio of the molar gas constant to Avogadro's number.

At absolute zero temperature, there is no thermal motion of the molecules and there is only one way to arrange the molecules, so there is only one microstate consistent with the macrostate, i.e. we are certain about the state of the molecules and

$$W = 1 \text{ and } S = 1.380658 \times 10^{-23} \ln 1 = 0$$

So the statistical thermodynamics definition of entropy proposed by Boltzmann agrees with that of Clausius at absolute zero temperature.

When the balloons are constrained in a box or net there are fewer configurations, perhaps two dozen ( $\ln 24 = 3.18$ ), that they can assume compared to the thousands of configurations ( $\ln 2000 = 7.6$ ) which they can assume when they are free to disperse around the room; thus their 'entropy' is higher in the dispersed state.

### Elaborate:

For an ideal gas the change in entropy between two states is given by

$$ds = c_p \ln \frac{T_2}{T_1} - R \ln \frac{P_2}{P_1}$$

where  $c_p$  (from thermodynamics tables<sup>1</sup>) is the specific heat capacity at constant pressure and  $R$  ( $=0.287$  kJ/kg·K) is the universal gas constant. Note that  $s$  is used to indicate specific entropy or entropy per unit mass.

We can consider air as an ideal gas and when it escapes from a puncture in our bicycle tire, the air experiences a change in entropy of

$$ds = c_p \ln \frac{T_2}{T_1} - R \ln \frac{P_2}{P_1} = 1.005 \ln \frac{290}{294} - 0.287 \ln \frac{101}{310} = 0.308 \text{ kJ/kg}\cdot\text{K}$$

assuming the temperature drops by 4°C from an ambient temperature of 21°C and the tires were pressurized at 45psi ( $\approx 310$  kPa). In other words, the air disperses taking its internal energy with it and this dispersion can be quantified by the increase in its entropy of 0.308 kJ/kg·K.

We can use Boltzmann's equation to calculate the increase in the number of macrostates present in 1 gram of escaping air, i.e.

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<sup>1</sup> e.g. <http://v5.sdsu.edu/testhome/Test/solve/basics/tables/tablesPG/pgConsts.html>

$$W = \exp \frac{s}{k} = \exp \left[ \frac{0.308 \times 10^{-3}}{1.380658 \times 10^{-23}} \right]$$

this is an enormous number of microstates which is beyond the range of the editor's calculator.

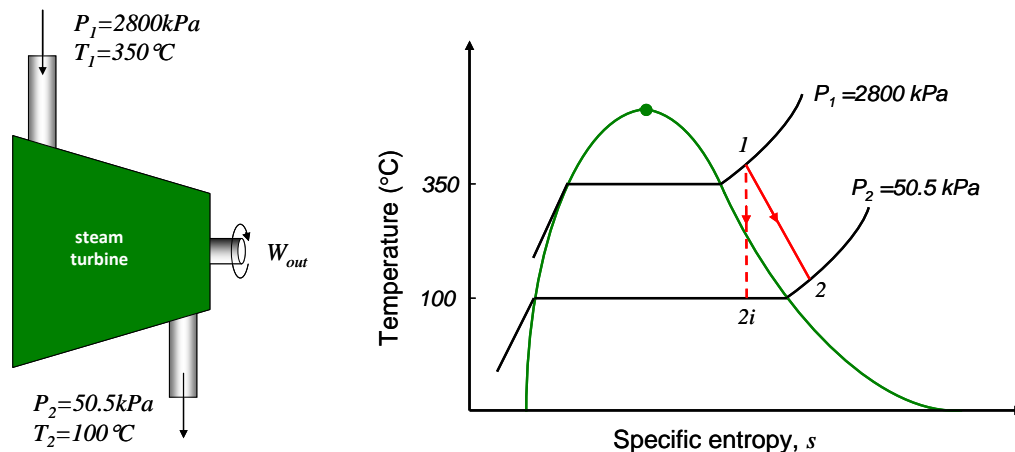
This tendency to disperse can be used to do work for us which is what happens in a turbine. For instance, steam is generated in a pressurized boiler (using a heat source derived from burning a fuel) at 2.8MPa and 420°C and is exhausted from the turbine at boiling point and half an atmosphere.

The entropy at the entry (1) and exit (2) states for the turbine can be found using the steam tables ([www.dofmaster.com/steam.html](http://www.dofmaster.com/steam.html)):

State 1:  $T_1 = 350^\circ\text{C}$  and  $P_1 = 2800\text{ kPa}$  so  $s_1 = 6.7842\text{ kJ/kg/}^\circ\text{C}$

State 2:  $T_2 = 100^\circ\text{C}$  and  $P_2 = 50.5\text{ kPa}$  so  $s_2 = 7.6905\text{ kJ/kg/}^\circ\text{C}$

These can be represented on a T-s diagram as shown below. In the ideal, reversible case there would be no increase in entropy and the process can be described as isentropic (constant entropy) resulting in end state  $2i$ .



For state  $2i$ :

$P_{2i} = P_2 = 50.5\text{ kPa}$  and  $s_{2i} = s_1 = 6.7842\text{ kJ/kg/}^\circ\text{C}$  from which the quality must be

determined: 
$$x_{2i} = \frac{s_{2i} - s_f}{s_{fg}} = \frac{6.7842 - 1.0941}{6.4972} = 0.8758$$

In order to define the efficiency of the turbine we need to introduce 'enthalpy'. Enthalpy is defined as the sum of the internal energy of the substance and the product of its pressure and volume, and can be expressed as  $h = u + pv$ . For state  $2i$ ,

$$h_{2i} = h_f + x_{2i}h_{fg}$$

where  $h_f$  and  $h_{fg}$  can be found in the steam tables for  $T_2 = 100^\circ\text{C}$  and  $P_2 = 50.5\text{ kPa}$ .

Hence,  $h_{2i} = h_f + x_{2i}h_{fg} = 341.6059 + (0.8758 \times 2304.7903) = 2360\text{ kJ/kg}$

The efficiency of the turbine can be defined as the ratio of the actual enthalpy change to the ideal (isentropic) enthalpy change, i.e.

$$\eta_{II} = \frac{h_1 - h_2}{h_1 - h_{2i}}$$

where  $h_1$  and  $h_2$  can be found in the steam tables i.e.

State 1:  $T_1 = 350^\circ\text{C}$  and  $P_1 = 2800\text{ kPa}$  so  $h_1 = 3121.86\text{ kJ/kg}$

State 2:  $T_2 = 100^\circ\text{C}$  and  $P_2 = 50.5\text{ kPa}$  so  $h_2 = 2682.5\text{ kJ/kg}$

hence 
$$\eta_{II} = \frac{h_1 - h_2}{h_1 - h_{2i}} = \frac{3121.86 - 2682.5}{3121.86 - 2360} = 0.577 \text{ or } 57.7\%$$

This is known as second-law efficiency and can be expressed in terms of useful work ( $W_{use}$ ) to reversible ( $W_{rev}$ ) work, i.e.  $\eta_{II} = W_{use}/W_{rev}$  for a work-performing device and  $\eta_{II} = W_{rev}/W_{use}$  for a work-consuming device.

### Evaluate:

Invite students to attempt the following examples:

#### Example 4.1

Determine the entropy generated when 1oz of milk from the refrigerator is added to an insulated 9oz mug of coffee. Where/what is this entropy?

#### Solution

Assume the refrigerator is at  $3^\circ\text{C}$  and the coffee at  $80^\circ\text{C}$  and that milk and coffee can be considered equivalent to water. The first law of thermodynamics can be used to consider the heat transfer that occurs during mixing in the absence of any external work or heat input; so that the heat transfer to the milk must equal the heat transfer from the coffee, i.e.

$$Q_{\text{gained by milk}} = Q_{\text{lost by coffee}} \quad \text{and} \quad Q = mc_p \Delta T$$

so the temperature,  $T_3$  after mixing without heat loss to the surroundings will be

$$T_3 = \frac{m_{\text{milk}} T_{\text{milk}} + m_{\text{coffee}} T_{\text{coffee}}}{m_{\text{milk}} + m_{\text{coffee}}} = \frac{(1 \times 276) + (9 \times 353)}{10} = 345.3\text{ K} (= 72.3^\circ\text{C})$$

The entropy generated will be  $S_{\text{generated}} = S_{\text{mixture}} - (S_{\text{milk}} + S_{\text{coffee}})$

Now, using the steam tables for water at  $T = 3, 80,$  and  $72.3^\circ\text{C}$ ,  $s = 0.0459, 1.0752,$  and  $0.9828\text{ kJ/kg}^\circ\text{C}$  respectively.

So, for milk before mixing,  $S_{\text{milk}} = m_{\text{milk}} s_{T=3} = 0.028349 \times 0.0459 = 1.3012 \times 10^{-3}\text{ kJ}$

for coffee before mixing,  $S_{\text{coffee}} = m_{\text{coffee}} s_{T=80} = 0.028349 \times 9 \times 1.0752 = 0.2743\text{ kJ}$

$$\text{for mixture, } S_{mixture} = m_{mixture} s_{T=72.3} = 0.028349 \times 10 \times 0.9828 = 0.2786 \text{ kJ}$$

hence the entropy generated is

$$S_{generated} = S_{mixture} - (S_{milk} + S_{coffee}) = 0.2786 - (0.0013 + 0.2743) = 3.0127 \times 10^{-3} \text{ kJ } (\approx 3 \text{ J})$$

### Example 4.2

Measure the temperature adjacent to the interior and external walls of your room; and calculate the entropy generation in the wall as a consequence of heat transfer through the wall.

### Solution

Solving this example for the editor's study in December in Michigan

$$T_{int} = 68^\circ\text{F} = 19.44^\circ\text{C} = 292.44 \text{ K}$$

$$T_{ext} = 28^\circ\text{F} = -2.22^\circ\text{C} = 270.78 \text{ K}$$

and  $\dot{Q}_{out} = h_c A (T_{room} - T_{environment})$

thus, if the coefficient of convective heat transfer<sup>6</sup>,  $h_c = 12 \text{ W}/(\text{m}^2 \cdot \text{K})$  and heat loss is through one wall to the outdoors ( $A = 2.7 \times 4.05 = 10.935 \text{ m}^2$ ) we have

$$\dot{Q}_{out} = 12 \times 10.935 (292.44 - 270.78) = 2842 \text{ W}$$

We can consider the wall to be a closed system since there is no mass transfer. Assuming the temperatures on each side of the wall to approximately constant (changing very slowly) then the rate of change of entropy across the wall is zero, i.e.

$$\frac{dS_{system}}{dt} = 0 = \dot{S}_{in} - \dot{S}_{out} + \dot{S}_{gen}$$

or  $\left(\frac{\dot{Q}}{T}\right)_{in} - \left(\frac{\dot{Q}}{T}\right)_{out} + \dot{S}_{gen} = 0$

so  $\dot{S}_{gen} = \frac{2842}{270.78} - \frac{2842}{292.44} = 0.778 \text{ W/K}$