

## 1.B: The Second Law of Thermodynamics

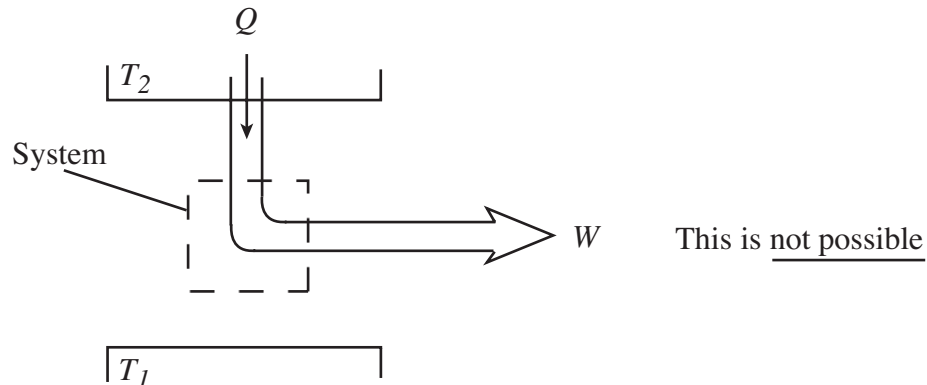
[IAW 42-50; VN Chapter 5; VWB&S-6.3, 6.4, Chapter 7]

### 1.B.1 Concept and Statements of the Second Law (Why do we need a second law?)

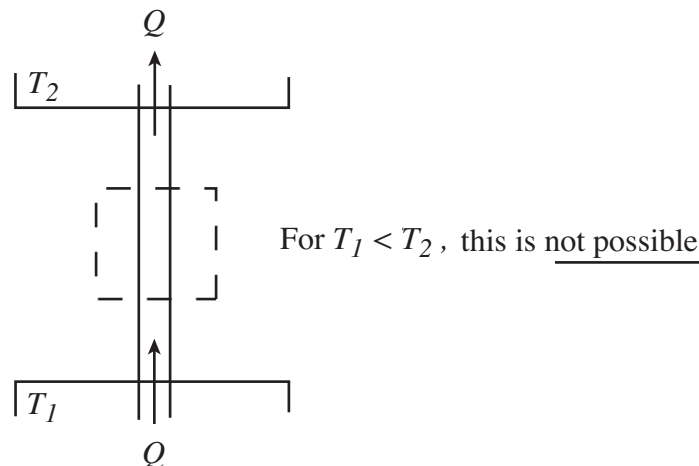
The unrestrained expansion, or the temperature equilibration of the two bricks, are familiar processes. Suppose you are asked whether you have ever seen the reverse of these processes take place? Do two bricks at a medium temperature ever go to a state where one is hot and one is cold? Will the gas in the unrestrained expansion ever spontaneously return to occupying only the left side of the volume? Experience hints that the answer is no. However, both these processes, unfamiliar though they may be, are compatible with the first law. In other words the first law does not prohibit their occurrence. There thus must be some other “great principle” that describes the direction of natural processes, that tells us which first law compatible processes will not be observed. This is contained in the second law. Like the first law, it is a generalization from an enormous amount of observation.

There are several ways in which the second law of thermodynamics can be stated. Listed below are three that are often encountered. As described in class (and as derived in almost every thermodynamics textbook), although the three may not appear to have much connection with each other, they are equivalent.

1) No process is possible whose *sole* result is the absorption of heat from a reservoir and the conversion of this heat into work. [Kelvin-Planck statement of the second law]



2) No process is possible whose *sole* result is the transfer of heat from a cooler to a hotter body. [Clausius statement of the second law]



3) There exists a property called **entropy**,  $S$ , which is a thermodynamic property of a system. For a reversible process, changes in this property are given by

$$dS = (dQ_{reversible})/T$$

The entropy change of any system and its surroundings, considered together, is positive and approaches zero for any process which approaches reversibility.

$$\Delta S_{total} \geq 0$$

For an *isolated system*, i.e., a system that has no interaction with the surroundings, changes in the system have no effect on the surroundings. In this case, we need to consider the system only, and the first and second laws become:

$$\begin{aligned} \Delta E_{system} &= 0 \\ \Delta S_{system} &\geq 0 \end{aligned}$$

For an isolated system the total energy ( $E = U + \text{Kinetic Energy} + \text{Potential Energy} + \dots$ ) is constant. The entropy can only increase or, in the limit of a reversible process, remain constant.

All of these statements are equivalent, but (3) gives a direct, quantitative measure of the departure from reversibility.

Entropy is not a familiar concept and it may be helpful to provide some additional rationale for its appearance. If we look at the first law,

$$dU = dQ - dW$$

the term on the left is a function of state, while the two terms on the right are not. For a simple compressible substance, however, we can write the work done in a reversible process as  $dW = PdV$ , so that

$$dU = dQ - PdV; \text{ First law for a simple compressible substance, reversible process.}$$

Two out of the three terms in this equation are expressed in terms of state variables. It seems plausible that we ought to be able to express the third term using state variables as well, but what are the appropriate variables? If so, the term  $dQ = ( ) [ ]$  should perhaps be viewed as analogous to  $dW = PdV$  where the parenthesis denotes an intensive state variable and the square bracket denotes an extensive state variable. The second law tells us that the intensive variable is the temperature,  $T$ , and the extensive state variable is the entropy,  $S$ .

The first law for a simple compressible substance in terms of state variables is thus

$$dU = TdS - PdV. \tag{B.1.1}$$

Because Eq. (B.1.1) includes the second law, it is referred to as the combined first and second law. Because it is written in terms of state variables, it is true for all processes, not just reversible ones.

We list below some attributes of entropy:

- a)  $S$  is an extensive variable. The entropy per unit mass, or specific entropy, is  $s$ .

- b) The units of entropy are Joules per degree Kelvin (J/K). The units for specific entropy are J/K-kg.
- c) For a system,  $dS = \frac{dQ_{rev}}{T}$ , where the numerator is the heat given to the system and the denominator is the temperature of the system at the location where the heat is received.
- d)  $dS = 0$  for pure work transfer.

### Muddy points

Why is  $dU = TdS - PdV$  always true? (MP 1B.1)

What makes  $dQ_{rev}$  different than  $dQ$ ? (MP 1B.2)

## 1.B.2 Axiomatic Statements of the Laws of Thermodynamics<sup>1</sup>

### (i.) Introduction

As a further aid in familiarization with the second law of thermodynamics and the idea of entropy, we draw an analogy with statements made previously concerning quantities that are closer to experience. In particular, we wish to (re-) present the Zeroth and First Laws of thermodynamics in the same framework as we have used for the Second Law. In this so-called "axiomatic formulation", the Zeroth, First and Second Laws are all introduced in a similar fashion.

### (ii.) Zeroth Law

We start with a statement which is based on two observations:

- a) If two bodies are in contact through a thermally-conducting boundary for a sufficiently long time, no further observable changes take place; thermal equilibrium is said to prevail.
- b) Two systems which are individually in thermal equilibrium with a third are in thermal equilibrium with each other; all three systems have the same value of the property called temperature.

The closely connected ideas of temperature and thermal equilibrium are formally expressed in the "Zeroth Law of Thermodynamics":

#### **Zeroth Law**

*There exists for every thermodynamic system in equilibrium a property called temperature. Equality of temperature is a necessary and sufficient condition for thermal equilibrium.*

The Zeroth law thus defines a property (temperature) and describes its behavior.

### (iii.) First Law

Observations also show that for any system there is a property called the energy. The First Law asserts that one must associate such a property with every system.

#### **First Law**

*There exists for every thermodynamic system a property called the energy. The change of energy of a system is equal to the mechanical work done on the system in an adiabatic process. In a non-adiabatic process, the change in energy is equal to the heat added to the system minus the mechanical work done by the system.*

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<sup>1</sup> From notes of Professor F. E. C. Culick, California Institute of Technology (with minor changes)

On the basis of experimental results, therefore, one is led to assert the existence of two new properties, the temperature and internal energy, which do not arise in ordinary mechanics. In a similar way, a further remarkable relationship between heat and temperature will be established, and a new property, the entropy, defined. Although this is a much less familiar property, it is to be stressed that the general approach is quite like that used to establish the Zeroth and First Laws. A general principle and a property associated with any system are extracted from experimental results. Viewed in this way, the entropy should appear no more mystical than the internal energy. The increase of entropy in a naturally occurring process is no less real than the conservation of energy.

#### (iv.) Second Law

Although all natural processes must take place in accordance with the First Law, the principle of conservation of energy is, by itself, inadequate for an unambiguous description of the behavior of a system. Specifically, there is no mention of the familiar observation that every natural process has in some sense a preferred direction of action. For example, the flow of heat occurs naturally from hotter to colder bodies, in the absence of other influences, but the reverse flow certainly is not in violation of the First Law. So far as that law is concerned, the initial and final states are symmetrical in a very important respect.

The Second Law is essentially different from the First Law; the two principles are independent and cannot in any sense be deduced from one another. Thus, the concept of energy is not sufficient, and a new property must appear. This property can be developed, and the Second Law introduced, in much the same way as the Zeroth and First Laws were presented. By examination of certain observational results, one attempts to extract from experience a law which is supposed to be general; it is elevated to the position of a fundamental axiom to be proved or disproved by subsequent experiments. Within the structure of classical thermodynamics, there is no proof more fundamental than observations. A statement which can be adopted as the Second Law of thermodynamics is:

#### **Second Law**

*There exists for every thermodynamic system in equilibrium an extensive scalar property called the entropy,  $S$ , such that in an infinitesimal reversible change of state of the system,  $dS = dQ/T$ , where  $T$  is the absolute temperature and  $dQ$  is the amount of heat received by the system. The entropy of a thermally insulated system cannot decrease and is constant if and only if all processes are reversible.*

As with the Zeroth and First Laws, the existence of a new property is asserted and its behavior is described.

#### (v.) Reversible Processes

In the course of this development, the idea of a completely reversible process is central, and we can recall the definition, "a process is called completely reversible if, after the process has occurred, both the system and its surroundings can be wholly restored by any means to their respective initial states". Especially, it is to be noted that the definition does not, in this form, specify that the reverse path must be identical with the forward path. If the initial states can be restored by any means whatever, the process is by definition completely reversible. If the paths are identical, then one usually calls the process (of the system) reversible, or one may say that the state of the system follows a reversible path. In this path (between two equilibrium states 1 and 2), (i) the system passes through the path followed by the equilibrium states only, and (ii) the system will take the reversed path 2 to 1 by a simple reversal of the work done and heat added.

Reversible processes are idealizations not actually encountered. However, they are clearly

useful idealizations. For a process to be completely reversible, it is necessary that it be quasi-static and that there be no dissipative influences such as friction and diffusion. The precise (necessary and sufficient) condition to be satisfied if a process is to be reversible is the second part of the Second Law.

The criterion as to whether a process is completely reversible must be based on the initial and final states. In the form presented above, the Second Law furnishes a relation between the properties defining the two states, and thereby shows whether a natural process connecting the states is possible.

### Muddy points

What happens when all the energy in the universe is uniformly spread, ie, entropy at a maximum? (MP 1B.3)

### 1.B.3 Combined First and Second Law Expressions

First Law:

$$dU = dQ - dW \text{ - Always true}$$

Work and heat exchange in terms of state variables:

$$dQ = TdS; \quad dW = PdV \text{ - Only true for reversible processes.}$$

$$dU = dQ - PdV \text{ ; Simple compressible substance, reversible process}$$

$$dU = dQ - PdV - XdY \text{ ; Substance with other work modes (e.g., stress-strain), X is a pressure-like quantity, Y is a volume like quantity}$$

$$dU = TdS - dW \text{ ; Only true for a reversible process}$$

First law in terms of state variables:

$$dU = TdS - PdV \text{ ; This is a relation between properties and is always true}$$

In terms of specific quantities (per unit mass):

$$du = Tds - Pdv \quad \textbf{Combined first and second law (a) or Gibbs equation (a)}$$

The combined first and second law expressions are often more usefully written in terms of the enthalpy, or specific enthalpy,  $h = u + Pv$ :

$$\begin{aligned} dh &= du + Pdv + vdP \\ &= Tds - Pdv + Pdv + vdP, \text{ using the first law.} \end{aligned}$$

$$dh = Tds + vdP$$

Or, since  $v = 1/\rho$

$$dh = Tds + \frac{dP}{\rho}. \quad \textbf{Combined first and second law (b) or Gibbs equation (b)}$$

In terms of enthalpy (rather than specific enthalpy) the relation is  $dH = TdS + VdP$ .

### 1.B.4 Entropy Changes in an Ideal Gas

Many aerospace applications involve flow of gases (e.g., air) and we thus examine the entropy relations for ideal gas behavior. The starting point is form (a) of the combined first and second law,

$$du = Tds - Pdv.$$

For an ideal gas,  $du = c_v dT$ . Thus

$$Tds = c_v dT + Pdv \quad \text{or} \quad ds = c_v \frac{dT}{T} + \frac{P}{T} dv.$$

Using the equation of state for an ideal gas ( $Pv = RT$ ), we can write the entropy change as an expression with only exact differentials:

$$ds = c_v \frac{dT}{T} + R \frac{dv}{v}. \quad (\text{B.4.1})$$

Integrating between two states “1” and “2”:

$$\Delta s = s_2 - s_1 = \int_{T_1}^{T_2} c_v \frac{dT}{T} + R \int_{v_1}^{v_2} \frac{dv}{v}.$$

For constant specific heat

$$\Delta s = s_2 - s_1 = c_v \ln\left(\frac{T_2}{T_1}\right) + R \ln\left(\frac{v_2}{v_1}\right).$$

In non-dimensional form (using  $\frac{R}{c_v} = (\gamma - 1)$ )

$$\frac{\Delta s}{c_v} = \ln\left(\frac{T_2}{T_1}\right) + (\gamma - 1) \ln\left(\frac{v_2}{v_1}\right). \quad \text{Entropy change of an ideal gas} \quad (\text{B.4.2})$$

Equation (B.4.2) is in terms of specific quantities. For N moles of gas

$$\frac{\Delta S}{C_v} = N \left[ \ln\left(\frac{T_2}{T_1}\right) + (\gamma - 1) \ln\left(\frac{V_2}{V_1}\right) \right].$$

Rather than temperature and volume, we can develop an alternative form of the expression, in terms of pressure and volume, for entropy change, which allows us to examine an assumption we have used over the past year. The ideal gas equation of state can be written as

$$\ln P + \ln v = \ln R + \ln T.$$

Taking differentials of both sides yields

$$\frac{dP}{P} + \frac{dv}{v} = \frac{dT}{T}$$

Using the above equation in Eq. (B.4.1), and making use of the relations  $c_p = c_v + R$ ;  $c_p/c_v = \gamma$ , we find

$$ds = c_v \left[ \frac{dP}{P} + \frac{dv}{v} \right] + R \frac{dv}{v},$$

or

$$\frac{ds}{c_v} = \frac{dP}{P} + \gamma \frac{dv}{v}.$$

Integrating between two states 1 and 2

$$\frac{\Delta s}{c_v} = \ln\left(\frac{P_2}{P_1}\right) + \gamma \ln\left(\frac{v_2}{v_1}\right) = \ln\left[\frac{P_2}{P_1} \left(\frac{v_2}{v_1}\right)^\gamma\right]. \quad (\text{B.4.3})$$

Using both sides of (B.4.3) as exponents we obtain

$$\frac{P_2 v_2^\gamma}{P_1 v_1^\gamma} = \left[ P v^\gamma \right]_1^2 = e^{\Delta s / c_v}. \quad (\text{B.4.4})$$

Equation (B.4.4) describes a general process. For the specific situation in which  $\Delta s = 0$ , i.e., the entropy is constant, we recover the expression  $P v^\gamma = \text{constant}$ . It was stated that this expression applied to a reversible, adiabatic process. We now see, through use of the second law, a deeper meaning to the expression, and to the concept of a reversible adiabatic process, in that both are characteristics of a constant entropy, or *isentropic*, process.

### **Muddy points**

Why do you rewrite the entropy change in terms of  $Pv^\gamma$ ? (MP 1B.4)

What is the difference between isentropic and adiabatic? (MP 1B.5)

### **1.B.5 Calculation of Entropy Change in Some Basic Processes**

a) Heat transfer from, or to, a heat reservoir.

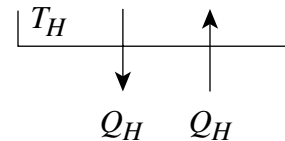
A heat reservoir is a constant temperature heat source or sink. Because the temperature is uniform, there is no heat transfer across a finite temperature difference and the heat exchange is reversible. From the definition of entropy ( $dS = dQ_{rev}/T$ ),

$$\Delta S = \frac{Q}{T},$$

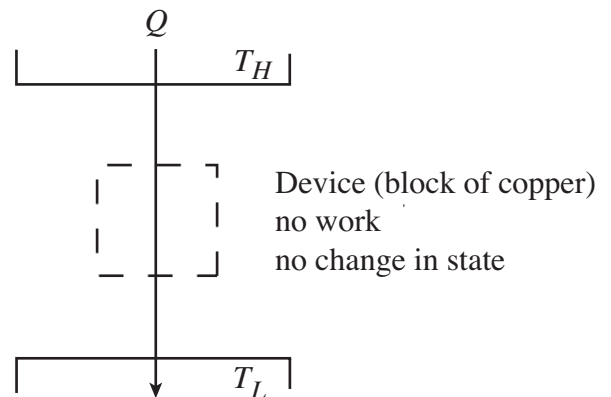
where  $Q$  is the heat into the reservoir (defined here as positive if heat flows into the reservoir)

b) Heat transfer between two heat reservoirs

The entropy changes of the two reservoirs are the sum of the entropy change of each. If the high temperature reservoir is at  $T_H$  and the low temperature reservoir is at  $T_L$ , the total entropy change is



Heat transfer from/to a heat reservoir



Heat transfer between two reservoirs

$$\Delta S = \left( \frac{-Q}{T_H} \right) + \left( \frac{Q}{T_L} \right) = \frac{Q}{T_H T_L} (T_H - T_L)$$

The second law says that the entropy change must be equal to or greater than zero. This corresponds to the statement that heat must flow from the higher temperature source to the lower temperature source. This is one of the statements of the second law given in Section 1.B.1.

### Muddy points

[In the single reservoir example, why can the entropy decrease? \(MP 1B.6\)9](#)

[Why does the entropy of a heat reservoir change if the temperature stays the same? \(MP 1B.7\)9](#)

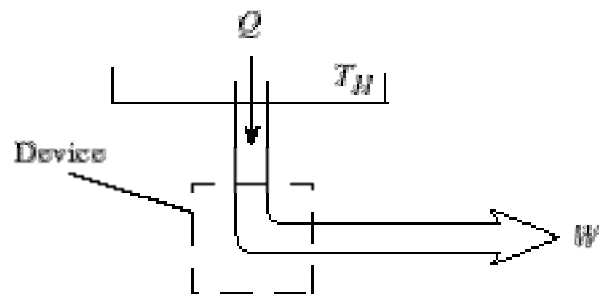
[How can the heat transfer from or to a heat reservoir be reversible? \(MP 1B.8\)9](#)

[How can  \$\Delta S\$  be less than zero in any process? Doesn't entropy always increase? \(MP 1B.9\)9](#)

[If  \$\frac{Q}{T} = \Delta S\$  for a reservoir, could you add  \$Q\$  to any size reservoir and still get the same  \$\Delta S\$ ? \(MP 1B.10\)](#)

### c) Possibility of obtaining work from a single heat reservoir

We can regard the proposed process as the absorption of heat,  $Q$ , by a device or system, operating in a cycle, rejecting no heat, and producing work. The total entropy change is the sum of the change in the reservoir, the system or device, and the surroundings. The entropy change of the reservoir is  $\Delta S = -Q/T_H$ . The entropy change of the device is zero, because we are considering a complete cycle (return to initial state) and entropy is a function of state. The surroundings receive work only so the entropy change of the surroundings is zero. The total entropy change is



Work from a single heat reservoir

$$\begin{aligned} \Delta S^{total} &= \Delta S_{reservoir} + \Delta S_{device} + \Delta S_{surroundings} \\ &= -Q/T_H + 0 + 0 \end{aligned}$$

The total entropy change in the proposed process is thus less than zero,

$$\Delta S^{total} < 0$$

which is not possible. The second law thus tells us that we cannot get work from a single reservoir only. The "only" is important; it means without any other changes occurring. This is the other statement of the second law we saw in Section 1.B.1.

### Muddy points

[What is the difference between the isothermal expansion of a piston and the \(forbidden\) production of work using a single reservoir? \(MP 1B.11\)](#)

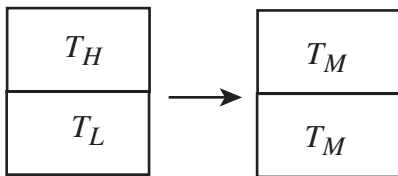
[For the "work from a single heat reservoir" example, how do we know there is no  \$\Delta S\_{surr}\$ ? \(MP 1B.12\)](#)



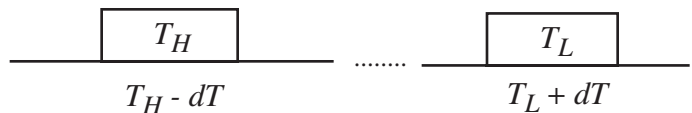
How does a cycle produce zero  $\Delta S$ ? I thought that the whole thing about cycles was an entropy that the designers try to minimize. (MP 1B.13)

d) Entropy changes in the “hot brick problem”

We can examine in a more quantitative manner the changes that occurred when we put the two bricks together, as depicted on the left-hand side of the figure below. The process by which the two bricks come to the same temperature is not a reversible one, so we need to devise a reversible path. To do this imagine a large number of heat reservoirs at varying temperatures spanning the range  $T_H - dT, \dots, T_L + dT$ , as in the right hand side of the figures. The bricks are put in contact with them sequentially to raise the temperature of one and lower the temperature of the



Temperature equalization of two bricks



Reservoirs used in reversible state transformation

other in a reversible manner. The heat exchange at any of these steps is  $dQ = CdT$ . For the high temperature brick, the entropy change is:

$$\Delta S_{hot\ brick} = \int_{T_H}^{T_M} \frac{CdT}{T} = C \ln\left(\frac{T_M}{T_H}\right)$$

where C is the heat capacity of the brick (J/kg). This quantity is less than zero. For the cold brick,

$$\Delta S_{cold\ brick} = \int_{T_L}^{T_M} \frac{CdT}{T} = C \ln\left(\frac{T_M}{T_L}\right).$$

The entropy change of the two bricks is

$$\Delta S^{bricks} = C \left[ \ln\left(\frac{T_M}{T_H}\right) + \ln\left(\frac{T_M}{T_L}\right) \right] = C \ln \frac{T_M^2}{T_H T_L} > 0.$$

The process is not reversible.

e) Difference between the free expansion and the reversible isothermal expansion of an ideal gas

The essential difference between the free expansion in an insulated enclosure and the reversible isothermal expansion of an ideal gas can also be captured clearly in terms of entropy changes. For a state change from initial volume and temperature  $V_1, T_1$  to final volume and (the same) temperature  $V_2, T_1$  the entropy change is

$$\Delta S = \int_1^2 dS = \int_1^2 \frac{dU}{T} + \int_1^2 \frac{PdV}{T},$$

or, making use of the equation of state and the fact that  $dU = 0$  for an isothermal process,

$$\Delta S = NR \ln\left(\frac{V_2}{V_1}\right).$$

This is the entropy change that occurs for the free expansion as well as for the isothermal reversible expansion processes—entropy changes are state changes and the two system final and end states are the same for both processes.

For the free expansion:

$$\Delta S^{\text{system}} = NR \ln\left(\frac{V_2}{V_1}\right); \quad \Delta S^{\text{surroundings}} = 0$$

There is no change in the entropy of the surroundings because there is no interaction between the system and the surroundings. The total entropy change is therefore,

$$\Delta S^{\text{total}} = \Delta S^{\text{system}} + \Delta S^{\text{surroundings}} = NR \ln\left(\frac{V_2}{V_1}\right) > 0.$$

There are several points to note from this result.

- i)  $\Delta S^{\text{total}} > 0$  so the process is not reversible
- ii)  $\Delta S^{\text{system}} > \int_1^2 \frac{dQ}{T} = 0$ ; the equality between  $\Delta S$  and  $\frac{dQ}{T}$  is only for a reversible process
- iii) There is a direct connection between the work needed to restore the system to the original state and the entropy change:

$$W = NRT \ln\left(\frac{V_2}{V_1}\right) = T\Delta S_{2-1}$$

The quantity  $T\Delta S$  has a physical meaning as “lost work” in the sense of work which we lost the opportunity to utilize. We will make this connection stronger in Section 1.C.

For the reversible isothermal expansion:

The entropy is a state variable so the entropy change of the system is the same as before. In this case, however, heat is transferred to the system from the surroundings ( $Q^{\text{surroundings}} < 0$ ) so that

$$\Delta S^{\text{surroundings}} = \frac{Q^{\text{surroundings}}}{T} < 0.$$

The heat transferred from the surroundings, however, is equal to the heat received by the system:

$$Q^{\text{surroundings}} = Q^{\text{system}} = W.$$

$$\Delta S^{\text{surroundings}} = \frac{Q^{\text{surroundings}}}{T} = \frac{-W}{T} = -NR \ln\left(\frac{V_2}{V_1}\right).$$

The total change in entropy (system plus surroundings) is therefore

$$\Delta S^{\text{total}} = \Delta S^{\text{system}} + \Delta S^{\text{surroundings}} = \frac{Q}{T} - \frac{Q}{T} = 0.$$

The reversible process has zero total change in entropy.

**Muddy points**

On the example of free expansion versus isothermal expansion, how do we know that the pressure and volume ratios are the same? We know for each that  $P_2 > P_1$  and  $V_2 > V_1$ . (MP 1B.14)

Where did  $\Delta S_{\text{system}} = NR \ln\left(\frac{V_2}{V_1}\right)$  come from? (MP 1B.15)

## Muddiest Points on Part 1B

### 1B.1 Why is $dU = TdS - PdV$ always true?

This is a relation between state variables. As such it is not path dependent, only depends on the initial and final states, and thus must hold no matter how we transition from initial state to final state. What is *not* always true, and what holds only for reversible processes are the relations  $Tds = dq$  and  $Pdv = dw$ . One example of this is the free expansion where  $dq = dw = 0$ , but where the quantities  $Tds$  and  $Pdv$  (and the integrals of these quantities) are not zero.

### 1B.2 What makes $dQ_{rev}$ different than $dQ$ ?

The term  $dQ_{rev}$  denotes the heat exchange during a reversible process. We use the notation  $dQ$  to denote heat exchange during *any* process, not necessarily reversible. The distinction between the two is important for the reason given above in (3).

### 1B.3 What happens when all the energy in the universe is uniformly spread, ie, entropy at a maximum?

I quote from *The Refrigerator and the Universe*, by Goldstein and Goldstein:

“The entropy of the universe is not yet at its maximum possible value and it seems to be increasing all the time. Looking forward to the future, Kelvin and Clausius foresaw a time when the maximum possible entropy would be reached and the universe would be at equilibrium forever afterward; at this point, a state called the “heat death” of the universe, nothing would happen forever after”. The book also gives comments on the inevitability of this fate.

### 1B.4 Why do you rewrite the entropy change in terms of $Pv^{\gamma}$ ?

We have discussed the representation of thermodynamic changes in  $P$ - $v$  coordinates a number of times and it is familiar, as is the idea of the “ $Pv^{\gamma} = \text{constant}$ ” process. I want to relate this to the more general expression involving the entropy change (Equation B.4.4) to show (i) when the simple form applied and (ii) how valid an approximation it was. Using the entropy change, we now have a quantitative metric for doing just that.

### 1B.5 What is the difference between isentropic and adiabatic?

Isentropic means no change in entropy ( $dS = 0$ ). An adiabatic process is a process with no heat transfer ( $dQ = 0$ ). We defined for **reversible** processes  $TdS = dQ$ . So generally an adiabatic process is not necessarily isentropic – only if the process is **reversible and adiabatic** we can call it isentropic. For example a real compressor can be assumed adiabatic but is operating with losses. Due to the losses the compression is irreversible. Thus the compression is not isentropic.

1B.6 In the single reservoir example, why can the entropy decrease?

When we looked at the single reservoir, our “system” was the reservoir itself. The example I did in class had heat leaving the reservoir, so that  $Q$  was negative. Thus the entropy change of the reservoir is also negative. The second law, however, *guarantees* that there is a positive change in entropy somewhere else in the surroundings that will be as large, or larger, than this decrease.

1B.7 Why does the entropy of a heat reservoir change if the temperature stays the same?

A heat reservoir is an idealization (like an ideal gas, a rigid body, an inviscid fluid, a discrete element mass-spring-damper system). The basic idea is that the heat capacity of the heat reservoir is large enough so that the transfer of heat in whatever problem we address does not appreciably alter the temperature of the reservoir. In grappling with approximations such as this it is useful to think about extreme cases. Therefore, suppose the thermal reservoir is the atmosphere. The mass of the atmosphere is roughly  $10^{19}$  kg (give or take an order of magnitude). Let us calculate the temperature rise due to the heat dumped into the atmosphere by a jet engine during a transcontinental flight. A large gas turbine engine might produce on the order of 100 MW of heat, so that the rise in atmospheric temperature,  $\delta T_{am}$ , for the heat transfer  $Q$  associated with a 6 hour flight is given by

$$M_{am}c_p\delta T_{am} = 6 \times 3600 \times 10^8 \text{ J}.$$

Substituting for the atmospheric mass and the specific heat gives a value for temperature change of roughly  $10^{-10}$  K. To a very good approximation, we can say that the temperature of this heat reservoir is constant and we can evaluate the entropy change of the reservoir as  $Q/T$ .

1B.8 How can the heat transfer from or to a heat reservoir be reversible?

We made the assumption that the heat reservoir is very large, and therefore it is a constant temperature heat source or sink. Since the temperature is uniform there is no heat transfer across a finite temperature difference and this heat exchange is reversible. We discussed this in the second example "Heat transfer between two heat reservoirs".

1B.9 How can  $\Delta S$  be less than zero in any process? Doesn't entropy always increase?

The second law says that the **total** entropy (system plus surroundings) always increases. (See Section 1.B.1). This means that **either** the system **or** the surroundings can have it entropy decrease if there is heat transfer between the two, although the sum of all entropy changes must be positive.

For an isolated system, with no heat transfer to the surroundings, the entropy must always increase.

1B.10 If  $\frac{Q}{T} = \Delta S$  for a reservoir, could you add  $Q$  to any size reservoir and still get the same  $\Delta S$ ?

Yes, as long as the system you were adding heat to fulfilled the conditions for being a reservoir.

1B.11 What is the difference between the isothermal expansion of a piston and the (forbidden) production of work using a single reservoir?

The difference is contained in the word **sole** in the Kelvin-Planck statement of the second law given in Section 1.B.1 of the notes.

For the isothermal expansion the changes are:

- a) The reservoir loses heat  $Q$
- b) The system does work  $W$  (equal in magnitude to  $Q$ )
- c) The system changes its volume and pressure.
- d) The system changes its entropy (the entropy increases by  $Q/T$ ).

For the “forbidden” process,

- a) The reservoir loses heat  $Q$
- b) The system does work  $W (= Q)$  and *that's all the changes that there are*. I leave it to you to calculate the total entropy changes (system plus surroundings) that occur in the two processes.

1B.12 For the "work from a single heat reservoir" example, how do we know there is no  $\Delta S_{sur}$ ?

Our system was the heat reservoir itself. In the example we had heat leaving the reservoir, thus  $Q$  was negative and the entropy change of the reservoir was also negative. Using the second law, it is guaranteed that somewhere else in the surroundings a positive entropy change will occur that is as large or larger than the decrease of the entropy of the reservoir.

1B.13 How does a cycle produce zero  $\Delta S$ ? I thought that the whole thing about cycles was an entropy that the designers try to minimize.

The change in entropy during a cycle is zero because we are considering a complete cycle (returning to initial state) and entropy is a function of state (holds for ideal and real cycles!).

The entropy you are referring to is entropy that is generated in the components of a non-ideal cycle. For example in a real jet engine we have a non-ideal compressor, a non-ideal combustor and also a non-ideal turbine. All these components operate with some loss and generate entropy – this is the entropy that the designers try to minimize. Although the change in entropy during a non-ideal cycle is zero, the total entropy change (cycle and

heat reservoirs!) is  $\Delta S_{\text{total}} > 0$ . Basically the entropy generated due to irreversibilities in the engine is additional heat rejected to the environment (to the lower heat reservoir). We will discuss this in detail in Section 1.C.1.

*1B.14 On the example of free expansion versus isothermal expansion, how do we know that the pressure and volume ratios are the same? We know for each that  $P_2 > P_1$  and  $V_2 > V_1$ .*

During the free-expansion no work is done and no heat is transferred (insulated system). Thus the internal energy stays constant and so does the temperature. This means that  $P_1 V_1 = P_2 V_2$  holds also for the free-expansion and that the pressure and volume ratios are the same when comparing free-expansion to reversible isothermal expansion.

*1B.15 Where did  $\Delta S_{\text{system}} = NR \ln\left(\frac{V_2}{V_1}\right)$  come from?*

We were using the 1<sup>st</sup> and 2<sup>nd</sup> law combined (Gibbs) and in the example discussed there was no change in internal energy ( $dU=0$ ). If we then integrate  $dS = P/TdV$  using  $P/T = NR/V$  (with  $N$  being the number of moles of gas in volume  $V$  and  $R$  is the universal gas constant) we obtain  $\Delta S_{\text{system}} = NR \ln(V_2/V_1)$ .