## 5 ENTROPY.

We have seen two empirical statements of the second law based on empirical observation.

(i) The statement due to Kelvin and Planck is that it is impossible to construct a device whose only action, when operating in a cycle, is to extract heat from a heat reservoir and to deliver an equivalent amount of work.

and

(ii) The statement due to Clausius that it was impossible to construct a device whose only action, when operating in a cycle, was to transfer heat from a cold to a hot reservoir.

We now need to look at this law and try to get it onto a more mathematical footing. This will involve the discovery of a new state function, entropy, and an examination of its basis around the exchange of heat between bodies. To do this we will need to start by continuing our study of the ideal (reversible) engine operating between two heat reservoirs.

So far we have considered engines operating on idealized cycles however real machines will interact with the environment to a lesser or greater extent as they exchange heat with many different bodies at many different temperatures. To investigate this exchange of heat we begin with reversible cycles before moving on to irreversible cycles.

## Clausius' Theorem.

Now that we have the tool of the Carnot cycle to aid understanding we may consider heat flow around a general cycle by starting with the reversible cycle as represented by the Carnot cycle.

We know already that for a Carnot cycle the heat flows and thermodynamic temperature are simply related as

$$\frac{Q_1}{Q_2} = \frac{T_1}{T_2} \qquad \qquad \Rightarrow \qquad \qquad \frac{Q_1}{T_1} = \frac{Q_2}{T_2}$$

We now envisage an arbitrary thermodynamic system undergoing a cycle including both heat flow and work processes and constrain all of the heat flows to be from a reversible Carnot engine operating from a hot reservoir at temperature  $T_0$  being used to drive an arbitrary system at temperature T by supplying incremental heat  $\delta Q(T)$  at that temperature to the system and causing it to do incremental work  $\delta W_{Sys}$ . This will involve the Carnot engine extracting incremental heat  $\delta Q(T_0)$  from the reservoir and doing incremental reversible work  $\delta W_{Rev}$  all shown in the figure.

NB. This can be generalized to a system where the temperature varies around the cycle by using multiple Carnot engines supplying the heat to the system at the appropriate temperature at any point around the system cycle.



Inside the dashed lines there is a composite system made up of the system under consideration and the Carnot engine whose inputs and outputs are  $dQ(T_0)$ ,  $dW_C$  and  $dW_{Sys}$ .

The quantities shown are then

1.  $dQ(T_0)$  is the heat received from the reservoir by the Carnot engine during one or more complete cycles of the Carnot engine.

2. dQ(T) is the heat rejected in one or more complete cycles of the Carnot engine consistent with constraints set by the requirements of the Carnot cycle,  $\frac{dQ(T_0)}{T_0} = \frac{dQ(T)}{T}$ 

3.  $dW_C$  is the work performed in one or more complete cycles by the Carnot engine consistent with constraints set by the requirements of the Carnot cycle,  $dW_C = dQ(T_0) - dQ(T)$ 

## 4. $dW_{Sys}$ is the increment of work performed by the system as it executes a cycle

First we note that  $dQ(T_0)$ , dQ(T) and  $dW_C$  are cyclical quantities wrt the Carnot engine but they are incremental quantities wrt the system.

First with regards to the Carnot engine we use the first law to obtain;

$$dW_C - dQ(T_0) + dQ(T) = 0$$

From our understanding of the Carnot cycle and the thermodynamic temperature scale;

$$\frac{T}{T_0} = \frac{dQ(T)}{dQ(T_0)}$$

Using these two equations we can eliminate  $dQ(T_0)$  and obtain

$$dW_C = \left(\frac{T_0}{T} - 1\right) dQ(T)$$

We next find the net work of the combined system and Carnot engine for one complete cycle

$$W_{Net} = \oint dW_C + \oint dW_{Sys}$$
  
System  
cycle  
System  
cycle

The second term on the RHS relates to dQ(T) via the first law applied to the system alone

$$\int dW_{Sys} = \int dQ(T)$$
System
System
Cycle
System
Cycle

We can now make substitutions to obtain

$$W_{Net} = \oint_{\substack{System \\ cycle}} \left[ \left( \frac{T_0}{T} - 1 \right) dQ(T) \right] + \oint_{\substack{System \\ cycle}} dQ(T)$$

Which simplifies to

$$W_{Net} = T_0 \oint_{\substack{System \\ cycle}} \frac{dQ(T)}{T}$$

If  $W_{Net}$  is positive we have a compound system that violates the Kelvin-Planck statement ie.a device would exist whose sole effect is the exchange of heat with a single reservoir and the creation of an equivalent amount of work.

If  $W_{Net}$  is negative or zero no principles are violated as we can always convert work completely to heat as did Joule in his experiments demonstrating the first law. Ie.

$$W_{Net} = T_0 \oint_{\substack{System \\ cycle}} \frac{dQ(T)}{T} \le 0$$

Since  $T_0$  is positive we have proved **THE CLAUSIUS INEQUALITY** 

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Whenever a system executes a complete cyclic process the integral of  $\frac{\delta Q}{T}$  around the cycle

is less than or equal to zero.

Otherwise stated as

$$\int_{\substack{System \\ cycle}} \frac{dQ(T)}{T} \le 0$$

For a reversible system cycle which we can go around in either sense with only the sign of the heat flow changing we have

$$\oint_{anticlockwise} \frac{dQ_R}{T} \le 0 \qquad \text{and} \qquad \oint_{clockwise} \frac{-dQ_R}{T} \le 0$$

This must mean that for a REVERSIBLE cycle

$$\oint_{Cycle} \frac{dQ_R}{T} = 0 \qquad \text{REVERSIBLE}$$

Then

$$\oint \frac{dQ}{T} < 0 \qquad \qquad \text{IRREVERSIBLE}$$

We note that the quantity  $\frac{dQ_R}{T}$  is behaving exactly as a state function where its integral over a cycle sums to zero, cf U, H, P and V

## Entropy

The significance of the Clausius inequality is still not apparent so let's consider a reversible cycle,  $Y_R$ 



For an arbitrary reversible cycle such as the one shown above, we can write the integral in two parts one for the upper and the other for the lower path such that

$$\int \frac{dQ_R}{T} = \int_{f_{upper}}^{i} \frac{dQ_R}{T} + \int_{i_{lower}}^{f} \frac{dQ_R}{T} = 0$$

Therefore,

$$\int_{i_{lower}}^{f} \frac{dQ_R}{T} = -\int_{f_{upper}}^{i} \frac{dQ_R}{T} = \int_{i_{upper}}^{f} \frac{dQ_R}{T}$$

But the lower and upper paths are any arbitrary paths connecting i to f and therefore the path integral of  $\frac{dQ_R}{T}$  is path independent (unlike the path integral of dQ alone which does depend on path) and this means that

$$\frac{dQ_R}{T}$$
 defines a new function of state (Like, P, V, U etc).

We call this function of state **THE ENTROPY**, **S**.

$$\Delta S \left( \equiv S_f - S_i \right) = \int_{i}^{f} \frac{dQ_R}{T}$$

## The state function *S* is a unique property of an equilibrium state.

It should be noted that with this definition only **ENTROPY DIFFERENCE** is unique. That is to say, entropy is only defined up to an arbitrary constant which could be taken to be the entropy of a reference state.

$$S_i = \int_{ref}^{i} \frac{dQ_R}{T} + S_{ref}$$

S has units of  $JK^{-1}$ .

Looking at differential change

 $dS = \frac{dQ}{T}$  and is a perfect differential (it must be as it is a state

function!). We now proceed to demonstrate this using our definition of a perfect differential.

## Example. Ideal Gas.

First Law states

 $dU = dQ_R - PdV$  (assuming a reversible process)

It follows that

$$dS = \frac{dQ_R}{T} = \frac{dU}{T} + \frac{P}{T}dV$$

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and from our equation of state we have

$$U = \frac{3}{2}PV \qquad PV = nRT \qquad \frac{P}{T} = \frac{nR}{V}$$
$$U = \frac{3}{2}nRT \Longrightarrow dU = \frac{3}{2}nRdT$$

So re-writing

$$dS = \frac{3}{2}nR\frac{dT}{T} + nR\frac{dV}{V} = a(V,T)dT + b(V,T)dV$$

with

$$a = \frac{3nR}{2T} \qquad \qquad b = \frac{nR}{V}$$

We see that we can use V and T as the natural variables of S (if V and T are both held constant the entropy is constant) and we can test for perfect differential status,

$$\frac{\partial a}{\partial V} = \frac{\partial}{\partial V} \left( \frac{3nR}{2T} \right) = 0 \qquad \qquad \frac{\partial b}{\partial T} = \frac{\partial}{\partial T} \left( \frac{nR}{V} \right) = 0$$

therefore

$$\frac{\partial a}{\partial V} = \frac{\partial b}{\partial T}$$

## Therefore dS is a perfect differential.

As we have already found S has V and T as natural variables and we may therefore write,

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV = \frac{3}{2} \frac{nR}{T} dT + \frac{nR}{V} dV$$

$$\left(\frac{\partial S}{\partial T}\right)_{V} = \frac{3}{2} \frac{nR}{T} \qquad \qquad \Rightarrow \qquad \qquad S = \frac{3}{2} nR \ln T + f(V)$$

and

$$\left(\frac{\partial S}{\partial V}\right)_T = \frac{nR}{V} \qquad \qquad \Rightarrow \qquad \qquad S = nR\ln V + g(T)$$

Both of these together give

$$S(V,T) = \frac{3}{2}nR\ln T + nR\ln V + const$$

For 1 mole of gas, n = 1

 $S \to \frac{S}{n} = s$  the molar entropy,  $C_V \to \frac{C_V}{n} = \frac{3}{2}R = c_v$  the **molar** specific heat

capacity at constant volume

$$s(v,T) = c_V \ln T + R \ln V + const$$

And

$$\Delta S = S(V_f, T_f) - S(V_i, T_i) = \frac{3}{2} nR \ln \left[\frac{T_f}{T_i}\right] + nR \ln \left[\frac{V_f}{V_i}\right]$$

(C)

## Examples of calculating S



 $S_{\rm f} - S_{\rm i}$  is uniquely defined as both states are equilibrium states. To calculate it we must consider any reversible path that will take us from i to f.



Make the change from 20 to  $100^{\circ}$ C in infinitesimal steps,

$$dS = \frac{dQ_R}{T} = mC_P \frac{dT}{T}$$

## Note that the changes are occurring at constant pressure.

Suppose the water has a mass m = 1 kg

$$\Delta S = mC_P \int_{293.16}^{373.16} \frac{dT}{T}$$

# NB. The temperature must be converted into degrees Kelvin for the calculation!!

 $C_P(\text{H}_2\text{O}) = 4.2 \times 10^3 \text{ JK}^{-1}\text{kg}^{-1}$ 

$$\Delta S_{H_2O} = 1kg \times 4.2 \times 10^3 JK^{-1}kg^{-1} \ln T \Big|_{29316}^{37316} = +1014 JK^{-1}$$

It is also instructive to calculate the change in the entropy of the reservoir where the temperature has remained constant.

$$\Delta S_{Res} = \int_{i}^{f} \frac{dQ_{Res}}{T} = \frac{1}{T_{f}} \int_{i}^{f} dQ_{Res} = \frac{1}{T_{f}} \left( Heat \ released \right) = -mC_{P}(H_{2}0) \frac{T_{f} - T_{i}}{T_{f}}$$

$$\Delta S_{Res} = -mC_P (H_2 0) \left( 1 - \frac{T_i}{T_f} \right) = -1kg \times 4.2 \times 10^3 J K^{-1} kg^{-1} \times \left( 1 - \frac{293.16}{373.16} \right) = -899 J K^{-1} \Delta S_{H_2O} + \Delta S_{Res} = (1014 - 899) J K^{-1} = 115 J K^{-1} > 0$$

## NB. Measurements of specific heats provide experimental methods for determining S.

## **Ex.2**

5kg of water at  $10^{\circ}$ C is mixed **adiabatically** with 2kg of water at  $40^{\circ}$ C.

First, what is the final equilibrium state? We need to find the final temperature.

The net heat change must be zero as the mixing is adiabatic.

Let the final temperature be T<sub>f</sub>

$$\Delta Q_{net} = 5kg \times 4.2 \times 10^3 (T_f - 283.16) + 2kg \times 4.2 \times 10^3 (T_f - 313.16) = 0$$

$$5 \times (T_f - 283.16) = -2 \times (T_f - 313.16)$$

$$7T_f = 5 \times 283.16 - 2 \times 313.16$$
  $T_f = \frac{5 \times 283.16 + 2 \times 313.16}{7} = 291.72K$ 

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$$\Delta S = \Delta S_{5kg} + \Delta S_{2kg} = 4.2 \times 10^3 (5kg \times \int_{283.16}^{T_f} \frac{dT}{T} + 2kg \times \int_{313.16}^{T_f} \frac{dT}{T})$$
$$\Delta S = 4.2 \times 10^3 \times \left(5\ln\frac{291.72}{283.16} + 2\ln\frac{291.72}{313.16}\right) = +30.7JK^{-1}$$

Ex.3

1kg of water is cooled from  $40^{\circ}$ C to  $20^{\circ}$ C, by placing a beaker outside in the garden, calculate  $\Delta S$  for the water and the surroundings.

$$dQ_R^{H_2O} = mC_P dT^{H_2O}$$

$$\Delta S_R^{H_2O} = mC_P \int_{313.16}^{293.16} \frac{dT}{T} = 1kg \times 4.2 \times 10^3 \ln \frac{293.16}{313.16} = -277 J K^{-1}$$

For the surroundings the temperature remained constant at 293.16K

$$\Delta S_{Surr} = \frac{1}{293.16} \times \Delta Q_{Surr} = \frac{-\Delta Q_{H_2O}}{293.16} = \frac{-1}{293.16} m C_P \int_{313.16}^{293.16} dT$$

$$\Delta S_{Surr} = \frac{-1}{293.16} \times 1kg \times 4.2 \times 10^3 \times (293.16 - 313.16) = 4.2 \times 10^3 \times \left(1 - \frac{313.16}{293.16}\right) = +286 \ JK^{-1}$$
  
$$\Delta S_{Net} = 286 \ JK^{-1} - 277 \ JK^{-1} = +9 \ JK^{-1} > 0$$

## Ex. 4

Mix 1kg of water at  $10^{0}$ C with 5kg of water at  $30^{0}$ C in an adiabatic enclosure

(i) What is the final state?

The final state is 6kg of water at T<sub>f</sub>. There is no heat input so;

$$\Delta Q(1 \text{kg}, 283.16 \text{K}) = 1 \times 4.2 \times 10^3 (283.16 - T_f)$$

 $\Delta Q(5\text{kg}, 303.16\text{K}) = 5 \times 4.2 \times 10^3 (303.16 - T_f)$ 

$$6T_f = (5 \times 303.16 + 283.16) \qquad T_f = 299.8K$$
$$\Delta S_{5kg} + \Delta S_{1kg} = 5 \times 4.2 \times 10^3 \int_{303.16}^{299.8} \frac{dT}{T} + 1 \times 4.2 \times 10^3 \int_{283.16}^{299.8} \frac{dT}{T}$$

$$\Delta S_{5kg} + \Delta S_{1kg} = 5 \times 4.2 \times 10^3 \times \ln \frac{299.8}{303.16} + 1 \times 4.2 \times 10^3 \times \ln \frac{299.8}{283.16} = -233JK^{-1} + 239JK^{-1}$$

 $\Delta S_{Tot} = +6JK^{-1}$ 

In summary, calculating  $\Delta S$  from heat flows eg.

$$\Delta S_{H_2O} = \int_{i}^{f} \frac{dQ}{T} = mC_P \int_{T_i}^{T_f} \frac{dT}{T} = mC_P \left[ \ln T_f - \ln T_i \right] mC_P \ln \frac{T_f}{T_i}$$

In general the specific heats will vary with temperature which complicates things if the variation is too large over the range of the temperature change. However we have ignored this effect.

**NB.** Since Entropy is a function of state it will change if the state changes with or without a flow of heat

## **Example Joule free expansion.**

We have met this before;



Where a gas is initially confined to one half of an adiabatic chamber and the partition is suddenly broken to allow unhindered expansion into the whole chamber with no flows of

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heat. This is an **irreversible process** with **no heat flows** and yet there will be a change of entropy.

$$\Delta S = S_f - S_i = \frac{3}{2}R\ln\frac{T_f}{T_i} + R\ln\frac{V_f}{V_i}$$

 $T_{\rm f} = T_{\rm i}$  (no heat flow and no work so no change in internal energy).

$$\Delta S = R \ln \frac{2V}{V} = R \ln 2 > 0$$

S has increased without any heat flow. In fact all of the examples we have seen so far have involved an increase of S from initial to final state value. And all examples have been irreversible.



What are we able to say about entropy change in irreversible processes? Consider the *PV* indicator diagram with the initial and final states i and f. There is shown an irreversible path from i to f and a reversible path from i to f.

From the Clausius inequality we can say that

$$\oint \frac{dQ}{T_{ext}} = \int_{i}^{f} \frac{dQ}{T_{ext}} + \int_{f}^{i} \frac{dQ_R}{T} \le 0$$

NB. When we use the Clausius inequality we need to distinguish between reversible and irreversible processes and the temperature used in the inequality. If the process is irreversible then the temperature is that of the external source supplying the heat to the system,  $T_{ext}$ , whereas in the case of a reversible process  $T_{ext} = T_{Sys} = T$  and no distinction is made. Recall that in the definition of dS based around this it is reversible heat flows that are the basis of the definition!

It follows that

$$\int_{i}^{f} \frac{dQ}{T_{ext}} \le -\int_{f}^{i} \frac{dQ_R}{T} = \int_{i}^{f} \frac{dQ_R}{T} = S_f - S_i = \Delta S$$

Whence for any change between equilibrium states i and f

$$\Delta S \ge \int_{i}^{f} \frac{dQ}{T_{ext}}$$
,  $dS \ge \frac{dQ}{T_{ext}}$  (Irreversible change)

$$\Delta S = \int_{i}^{f} \frac{dQ_R}{T} \qquad \qquad dS = \frac{dQ_R}{T} \qquad (\text{Reversible change})$$

Consider a thermally isolated system, AQ = 0

Then clearly from the above inequality

 $\Rightarrow \Delta S \ge 0 \qquad dS \ge 0 \qquad \text{(Thermally isolated system)}$ 

For a reversible change

$$\Delta S = 0$$
  $dS = 0$  (Reversible change in thermally isolated system)

## In summary;

1) The entropy of a thermally isolated system can only increase or remain constant.

2) Spontaneous changes in isolated systems lead to an increase in entropy.

3) In a thermally isolated system, S will tend to the maximum value possible

4) In a totally isolated system, S will tend to the maximum possible value at fixed U ie. U will remain constant.

## These are all;

## ENTROPY STATEMENTS OF

## THE SECOND LAW OF THERMODYNAMICS

Clearly, we should consider the combination of our system (under study) plus the surroundings plus everything else as a closed and thermally isolated system and therefore, for any change that occurs, the grand statement can be made that



And the equality part of this statement only pertains if the change is reversible.

Ex.



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A mass, *m*, of water at an initial temperature,  $T_i$ , is placed in thermal contact with a reservoir at temperature  $T_R$  and the water temperature approaches that of the reservoir irreversibly until it reaches a final temperature,  $T_f = T_R$ .

$$\Delta S_{system} = mC_P \ln\left[\frac{T_f}{T_i}\right]$$

And

$$\Delta S_{reservoir} = \int_{i}^{f} \frac{dQ_R}{T} = \frac{1}{T_f} \int_{i}^{f} dQ_R = \frac{\Delta Q_R}{T_f} = -\frac{mC_P}{T_f} \left(T_f - T_i\right)$$

We can say nothing about the respective signs of the entropy changes as we do not specify whether  $T_i$  is greater or less than the reservoir temperature although we can say that they have opposite signs. It is important to stress at this point that they do not have equal magnitudes (*entropy is not a conserved quantity*!!).

We seek a more general statement.

$$\Delta S_{Universe} = \Delta S_{System} + \Delta S_{reservoir}$$

$$\Delta S_{Universe} = mC_P \ln\left(\frac{T_f}{T_i}\right) - mC_P \left(1 - \frac{T_i}{T_f}\right) = -mC_P \ln\left(\frac{T_i}{T_f}\right) - mC_P \left(1 - \frac{T_i}{T_f}\right)$$
$$\Delta S_{Universe} = -mC_P \ln\left[1 - \left(1 - \frac{T_i}{T_f}\right)\right] - mC_P \left(1 - \frac{T_i}{T_f}\right)$$

This is in the form

$$\Delta S_{Universe} = -mC_P \ln(1-X) - mC_P X$$

where

$$X = \left(1 - \frac{T_i}{T_f}\right)$$

Note that

for cooling,  $\frac{T_i}{T_f} > 1$  and X < 0 is negative,

for warming,  $\frac{T_i}{T_f} < 1$  and 0 < X. < 1

Using McClaurens series expansion,  $-ln(1-x) = x + \frac{x^2}{2} + \frac{x^3}{3} + \dots$ 

$$\Delta S_{Universe} = mC_P \left[ X + \frac{X^2}{2} + \frac{X^3}{3} + \dots - X \right] = mC_P \left[ \frac{X^2}{2} + \frac{X^3}{3} + \dots \right]$$

# Note, $\Delta S_{\text{Universe}}$ has increased only when X > 0 ie only with the water warming ie. Is not independent of the sign of *X*! SOMETHING WRONG HERE???

This is now our mathematical expression of the second law of thermodynamics previously formulated as statements grounded in empirical observation.

How does the inequality,  $\Delta S \ge 0$  relate to those previous statements.

a) Kelvin's statement was that heat could not be converted into work with 100% efficiency, or equivalently that some heat must always be ejected as waste from the engine into a cold reservoir. We can relate this to the new form of the second law by asking what happens to entropy if we can convert heat to work with no waste heat being rejected to a cold reservoir. The heat has come **from** a hot body and therefore involves a **decrease in the entropy of that body** (the hot reservoir)

$$\Delta S_{Res} = -\frac{\int dQ}{T_1} = -\frac{Q_1}{T_1} < 0$$

(where we have used the same notation as in our discussion on engines). For the system operating in a cycle

$$\Delta S_{Sys} = \oint_{cycle} \frac{dQ}{T} = 0$$

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Ie. if there is only work then performed which of itself has no effect on the entropy of the system or universe the second law as an inequality is violated, entropy has been reduced.

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$$\Delta S_{Universe} = \Delta S_{Res} + \Delta S_{Sys} = -\frac{\int dQ}{T_1} = -\frac{Q_1}{T_1} < 0$$

We can see now that the "waste" heat rejected into the cold reservoir in any real engine is absolutely necessary in order that the second law is complied with ie. It acts to raise

that body's entropy by an amount  $\Delta S = \frac{\int dQ}{T_2} = \frac{Q_2}{T_2}$  such that

$$\Delta S_{univese} = -\frac{Q_1}{T_1} + \frac{Q_2}{T_2} > 0$$

Ie the entropy is increased and because **the heat came from a hot body** and was **rejected to a colder body**, from our measure of entropy where the temperature of the body appears in the denominator, this allows a smaller amount of heat  $Q_2 < Q_1$  to be rejected to the colder body but still for there to be a greater entropy increase to allow full compliance with the second law and yet leave some energy,  $Q_1 - Q_2$  from the hot body to be available to perform useful work, *W*.

**b) Clausius' statement** that heat could not flow spontaneously from a colder to a hotter body can be related to the new entropic second law by imagining the scenario, breaking Clausius' statement, where a glass of water is placed in a warm oven and ice forms spontaneously as the colder body, the water , loses heat to the warmer body, the oven. The water as it cools loses heat and will see a decrease in its entropy

 $\Delta S_{H_2O} = -\frac{\int dQ}{T_{H_2O}} = -\frac{\Delta Q}{T_{H_2O}}$  whilst the warmer oven receiving the heat will see an

increase in its entropy of  $\Delta S_{Oven} = +\frac{\int dQ}{T_{Oven}} = +\frac{\Delta Q}{T_{Oven}}$ . We see immediately that the

occurrence of the temperature in the denominator of these expressions means that the same amount of heat has transferred from the water and to the oven and yet the negative change in entropy for the colder water is much larger than it is for the warmer oven and

$$\Delta S_{Universe} = \frac{\Delta Q}{T_{Oven}} - \frac{\Delta Q}{T_{H_2O}} = \Delta Q \left( \frac{T_{H_2O} - T_{Oven}}{T_{H_2O} T_{Oven}} \right) < 0$$

The second law in its entropic form is again violated. Heat cannot therefore leave a colder body and flow to a hotter body as this will inevitable lead to a decrease in entropy in contravention of the entropic forms of the second law.

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As a thought experiment we could consider the warming of the water reversibly by using the heat output of a Carnot engine taking an infinitesimal heat,  $dQ_1$  from a heat reservoir and delivering an infinitesimal amount,  $dQ_2$  to the water whilst doing work dW and running many cycles, see diagram below.



For a Carnot engine we know

$$\frac{dQ_1}{-dQ_2} = \frac{T_1}{T_2} \qquad \Rightarrow \qquad \frac{dQ_2}{T_2} = -\frac{dQ_1}{T_1}$$

therefore

$$\frac{dQ_2}{T_2} + \frac{dQ_1}{T_1} = 0$$

$$dS_2 + dS_1 = 0$$

$$dS_{Universe} = 0 \qquad \Rightarrow \qquad \Delta S_{Universe} = \int dS = 0$$

In that example we required that the initial and final states are equilibrium states. We are able to relax this requirement slightly.

Suppose a system is not in complete equilibrium but it can be conceptually subdivided into small but macroscopic parts each of which can individually be regarded as in equilibrium at it's own temperature, pressure and volume.



## **Temperature gradient**



In the above, the system is in local equilibrium but will not reach total equilibrium until the entire system is uniform including T and P.

We can still define initial values of quantities like U and S as follows

$$U_{initial} = \sum_{i} U_{i} \qquad \qquad S_{initial} = \sum_{i} S_{i}$$

Our recently discovered results will then apply to the spontaneous irreversible change whereby the temperature and pressure come to uniformity.

ie. we will still have;

$$S_f - S_i = \Delta S \ge 0$$

We can use the function of state *S* to re-express the first law in its infinitesimal form as;

$$dU = dQ_R + dW_R = dQ_R - PdV$$

And this can be re-expressed as

$$dU = TdS - PdV$$

# But the second of the two expressions of the first law contains only functions of state or their changes, dU, dS, dV, T and P!

This is known as

## THE THERMODYNAMIC IDENTITY

Therefore this equation is an identity for any two equilibrium states infinitesimally close.

All differentials in this identity are now perfect differentials, independent of path!

$$dU = TdS - PdV = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV$$
$$\Rightarrow U = U(S, V)$$

and

$$\left(\frac{\partial U}{\partial S}\right)_V = T \qquad \qquad \left(\frac{\partial U}{\partial V}\right)_S = -P$$

Or we can look at it another way

$$dS = \frac{1}{T}dU + \frac{P}{T}dV = \left(\frac{\partial S}{\partial U}\right)_{V}dU + \left(\frac{\partial S}{\partial V}\right)_{U}dV$$

$$\Rightarrow$$
  $S = S(U, V)$ 

and

$$\left(\frac{\partial S}{\partial U}\right)_{V} = \frac{1}{T} \qquad \qquad \left(\frac{\partial S}{\partial V}\right)_{U} = \frac{P}{T}$$

Relations such as these relating partial differentials to physical quantities will often prove useful as we shall see when looking at the physical meaning of entropy.

## **Extensive and Intensive variables.**

*S*, *U* and *V* all **depend on the size of the system** (number of moles) for a given equilibrium state. If the size is doubled then each of *S*, *U* and *V* is also doubled. Variables that have this property are called **EXTENSIVE** thermodynamic variables.

Quantities such as P and T are **independent of system size** and are called **INTENSIVE** thermodynamic variables.

It is possible to show that **AT EQUILIBRIUM**, for a **TOTALLY ISOLATED SYSTEM**, the temperature and pressure (any intensive variables) must be **UNIFORM** throughout the system.

Ex.

1	2
U <sub>1</sub>	$U_2$

**Totally Isolated** 

## Heat Conducting Walls

 $S = S_1 + S_2 = S_1(U_1, V_1) + S_2(U_2, V_2)$  (All are extensive variables)

$$U = U_1 + U_2 = constant$$
 ie, U is extensive

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For equilibrium *S* must be a MAXIMUM even though energy exchange can occur through the walls.

$$dU = dU_1 + dU_2 = 0 \Rightarrow dU_1 = -dU_2$$

We may then say that

$$\frac{\partial S}{\partial U_1} = \frac{\partial S_1}{\partial U_1} + \frac{\partial S_2}{\partial U_1} = \frac{\partial S_1}{\partial U_1} - \frac{\partial S_2}{\partial U_2} = 0$$

Or equivalently

$$\frac{1}{T_1} - \frac{1}{T_2} = 0 \qquad \qquad T_1 = T_2 \qquad \text{ie. T is intensive.}$$

Suppose 1 and 2 are at the same temperature but are separated by a moveable piston



**Totally Isolated** 

## **Heat Conducting Walls**

$$S = S_1 + S_2 = S_1(U_1, V_1) + S_2(U_2, V_2)$$

 $V = V_1 + V_2 = constant$ 

$$dV = dV_1 + dV_2 = 0 \implies dV_2 = -dV_1$$

We may then say that

$$\frac{\partial S}{\partial V_1} = \frac{\partial S_1}{\partial V_1} + \frac{\partial S_2}{\partial V_1} = \frac{\partial S_1}{\partial V_1} - \frac{\partial S_2}{\partial V_2} = 0$$

Or equivalently

 $\frac{P_1}{T} - \frac{P_2}{T} = 0 \qquad \Rightarrow \qquad P_1 = P_2 \qquad \text{(it is intensive as we also)}$ 

found for *T*.)

## THE MICROSCOPIC INTERPRETATION OF ENTROPY

So far we have developed the idea of entropy from an empirical viewpoint beginning with the statements of Clausius and Kelvin-Joule which were based on observation, heat doesn't run from cold to hot objects and work cannot be obtained from heat with 100% efficiency. From this we have found a new state function whose value can be determined (up to a constant) from measurements of specific heat;

$$C_V = \lim_{\Delta T \to 0} it \left(\frac{\Delta Q_R}{\Delta T}\right)_V = \lim_{\Delta T \to 0} it \left(\frac{T\Delta S}{\Delta T}\right)_V = T \left(\frac{\partial S}{\partial T}\right)_V = \left(\frac{\partial S}{\partial \ln T}\right)_V$$

$$C_P = \lim_{\Delta T \to 0} it \left(\frac{\Delta Q_R}{\Delta T}\right)_P = \lim_{\Delta T \to 0} it \left(\frac{T\Delta S}{\Delta T}\right)_P = T \left(\frac{\partial S}{\partial T}\right)_P = \left(\frac{\partial S}{\partial \ln T}\right)_P$$

By measuring either  $C_V$  or  $C_P$  we may determine S by integration.

What we need to ask now is whether there is a microscopic understanding of entropy analogous to our microscopic understanding of temperature and its relationship to microscopic kinetic energy. We would like to have an intuitive understanding of such features as the fact that for an isolated system *S* always increases or remains constant but never decreases.

Ludwig Boltzmann was the first to give such a microscopic explanation of entropy. We may express Boltzmann's conjecture in this way;

Entropy is a measure of the MICROSCOPIC probability of finding the system under study in a given MACROSCOPIC equilibrium state.

By probability we mean here a number that is proportional to the number of distinct ways a system can arrange itself microscopically to achieve a particular macroscopic equilibrium state.

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We can put this idea on a firmer footing with the help of an example. Imagine a simple fluid or gas system with fixed volume, V and internal energy, U. V and U are independent state functions and as such are sufficient to define a macroscopic equilibrium state uniquely. Let us introduce

 $\Omega(U,V)$  = number of distinct microscopic arrangements of the system giving the same U and V. If that is so then the entropy S is some function of  $\Omega(U,V)$ .

$$S(U,V) = f(\Omega)$$

To have a better understanding of what is signified by  $\Omega$ , consider the gas in question to be dilute. Microscopically the state of the gas is described by giving the values of the **position** and **momentum** of every molecule. If the position or momentum of a single molecule is altered we change the **microscopic state** of the gas.

We begin by asking how many ways there are of arranging the positions of the atoms of the gas in a volume *V*.

To begin to answer this we need to give the atoms some choices. To do this, imagine dividing up the volume *V* into little cubes or cells of side length  $\Delta X$ . The number of cells is then

$$N = \frac{V}{(\varDelta X)^3}$$

This is the number of places we can put one molecule. The next molecule can also go into N places and so on giving us

$$\Omega_{Position} = \frac{V}{(\Delta X)^3} \times \frac{V}{(\Delta X)^3} \times \frac{V}{(\Delta X)^3} \times \frac{V}{(\Delta X)^3} \dots \frac{V}{(\Delta X)^3}$$
$$\Omega_{Position} = \left(\frac{V}{(\Delta X)^3}\right)^N$$

Next, we need to look at the number of ways the momenta can be arranged.

Recall,

$$U = N \left\langle \frac{1}{2} m v^2 \right\rangle = N \frac{\left\langle p^2 \right\rangle}{2m} = N \frac{p_{rms}^2}{2m}$$

and

$$p_{rms} = \sqrt{2m\frac{U}{N}}$$

The momentum is to be spread over a region of side  $p_{rms}$  in momentum space. As with our earlier argument about position and arrangements we can divide this momentum space up into infinitesimal cells or cubes of side  $\Delta p$  and the number of choices is

$$N_p = \frac{p_{rms}^3}{(\Delta p)^3}$$

And the number of arrangements is

$$\Omega_{Momentumn} = \left(\frac{p_{rms}^3}{(\Delta p)^3}\right)^N$$

The total number of arrangements is the product of these two numbers

$$\Omega(U,V) = \Omega_{Space} \,\Omega_{Momentum} = \left(\frac{V}{(\Delta X)^3}\right)^N \left(\frac{p_{rms}^3}{(\Delta p)^3}\right)^N$$

$$\Omega(U,V) = \left(\frac{V p_{rms}^3}{(\Delta X \Delta p)^3}\right)^N$$

Up until now in this argument we have assumed that all of the particles are distinguishable which of course they are not

Ie. we have treated arrangements like the six shown below as distinguishable, that is, as separate microscopic arrangements.

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They are clearly identical and because we have three boxes and 3 numbers there are 3! = 6 of these equivalent arrangements. For *N* identical particles we should divide our first naive answer by N!

$$\Omega_{Identical}(U,V) = \frac{1}{N!} \left( \frac{V p_{rms}^3}{(\Delta X \Delta p)^3} \right)^N$$

The next problem to be dealt with is how can we find what the function  $f(\Omega)$  should be like in order that it gives us the entropy or something with similar properties. One important property that we know is that *S* is extensive ie. additive.

U <sub>1</sub>	$U_2$	$U = U_1 + U_2$
$V_1$	$\mathbf{V}_2$	$V = V_1 + V_2$

$$S(U,V) = S_1(U_1,V_1) + S_2(U_2,V_2)$$

But, also in the above diagram we know that each of the two subsystems has its own number of arrangements,  $\Omega_1(U_1, V_1)$  and  $\Omega_2(U_2, V_2)$ . We also know that for the combined system the number of arrangements is given by the product!

$$\Omega = \Omega_1 \Omega_2$$

Together with

$$S = f(\Omega) = f(\Omega_1 \Omega_2) = S_1 + S_2 = f(\Omega_1) + f(\Omega_2)$$

The function we seek then has the property

$$f(\Omega_1 \Omega_2) = f(\Omega_1) + f(\Omega_2)$$

We can suggest a function that assigns this additive property to a product as we know that

$$ln(ab) = ln a + ln b$$

More generally we conclude that

$$S = C_2 ln \Omega + C_1$$

where we include the constant  $C_1$  to give us the most general form.

Checking the properties are those of an extensive quantity,

$$S = S_1 + S_2 = C_2(\ln \Omega_1 + \ln \Omega_2) + C_1 = C_2 \ln(\Omega_1 \Omega_2) + C_1 = S_1 + S_2 = C_2 \ln(\Omega_1 \Omega_2) + C_1 = S_1 + S_2 = C_2 \ln(\Omega_1 \Omega_2) + C_1 = S_1 + S_2 = C_2 \ln(\Omega_1 \Omega_2) + C_1 = S_1 + S_2 = C_2 \ln(\Omega_1 \Omega_2) + C_1 = S_1 + S_2 = C_2 \ln(\Omega_1 \Omega_2) + C_1 = S_1 + S_2 = C_2 \ln(\Omega_1 \Omega_2) + C_1 = S_1 + S_2 = S_2 + S_2 = S_1 + S_2 = S_2 + S_2 + S_2 = S_2 + S_2$$

As we know *S* to a constant we can choose to define S = 0 when  $\Omega = 1$  and thus  $C_1 \equiv 0$ 

ie. We can make the arbitrary choice that S is lowest when there is only one arrangement that will give rise to the macrostate!

This still leaves us to find  $C_2$ .

The argument for the form of  $f(\Omega)$  can be made in a mathematically more formal way and this is presented in an appendix to this set of notes.

<u>To find the constant  $C_2$  we return to the dilute gas</u>

$$S(U,V) = C_2 \ln \Omega_{Identical}$$

$$\ln \Omega_{Identical} = \ln \left[ \frac{1}{N!} \left( \frac{V p_{rms}^3}{(\Delta X \Delta p)^3} \right)^N \right] = N \ln \left( \frac{V p_{rms}^3}{(\Delta X \Delta p)^3} \right) - \ln N!$$

We can use the fact that

$$\ln N! \approx N \ln N - N$$

And that

$$p_{rms} = \left(\frac{2mU}{N}\right)^{1/2}$$

to obtain

$$\ln \Omega_{Identical} = N \ln \left( V \left( \frac{2mU}{N} \right)^{3/2} \right) - N \ln N + N - N \ln \left( (\Delta X \Delta p)^{3} \right)$$

$$\ln \Omega_{Identical} = N \ln V - N \ln N + \frac{3}{2} N \ln \left(\frac{U}{N}\right) + N + N \ln \left(\frac{(2m)^{3/2}}{(\Delta X \Delta p)^3}\right)$$

$$\ln \Omega_{Identical} = N \ln \left(\frac{V}{N}\right) + \frac{3}{2} N \ln \left(\frac{U}{N}\right) + terms \ independent \ of \ U \ or \ V$$

$$S(U,V) = C_2 N \ln\left(\frac{V}{N}\right) + \frac{3}{2}C_2 N \ln\left(\frac{U}{N}\right) + \cos t ant$$

We found previously that  $\left(\frac{\partial S}{\partial U}\right)_V = \frac{1}{T}$  which can now be used to finish this derivation

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_V = \frac{3}{2}C_2\frac{N}{U} \Longrightarrow U = \frac{3}{2}C_2NT$$

For 1 mole

$$U = \frac{3}{2}RT = \frac{3}{2}N_A k_B T = \frac{3}{2}C_2 N_A T$$

Gives us  $C_2$ 

$$C_2 = \frac{R}{N_A} = k_B$$

$$S(U,V)=k_{\rm B}\ln\Omega(U,V)$$

We can see now why *S* may increase even in the absence of heat flow when the system can spontaneously pass from a **LESS PROBABLE** (small  $\Omega$ ) to a **MORE PROBABLE** (large  $\Omega$ ) state. It may never find its way back to the less probable original state and continue evolving to states which are available with more ways of achieving them.

This microscopic explanation of entropy due to Ludwig Boltzmann was never accepted in his lifetime and this was understood to be the main reason behind is suicide.

Today on his tombstone are inscribed the letters

## S = klogW

The Boltzmann microscopic theory of entropy should offer predictions that fall into agreement with the macroscopic theory found earlier

Consider as an example JOULE EXPANSION

Take 1 mole of an ideal gas ( $N = N_A$ ) in a box divided into two identical halves each of value *V*. Start with all of the gas in the left hand half of the box confined by a membrane with a vacuum to the right. Break the membrane to produce a free expansion into a volume 2V





## Before

After

After the expansion the number of arrangements of the atoms is changed from  $\Omega(V)$  to  $\Omega(2V)$ . The  $N_A$  atoms each now have twice as many choices than initially as they have twice the volume they may occupy

$$\Omega(2V) = 2 \times 2 \times 2 \times \dots \times 2 \times \Omega(V) = 2^{N_A} \Omega(V)$$

$$S(2V) = k_B \ln \Omega(2V) = k_B \ln 2^{N_A} \Omega(V)$$
$$S(2V) = k_B \ln 2^{N_A} + k_B \ln \Omega(V)$$

$$S(2V) = k_B N_A \ln 2 + S(V)$$

And finally the change in entropy is

$$\Delta S = S(2V) - S(V) = k_B N_A \ln 2 = R \ln 2$$

But from the earlier macroscopic argument we had,

$$\Delta S = S(2V) - S(V) = nR \ln \frac{V_2}{V_1} = R \ln 2$$

As n = 1 and  $V_2 = 2V_1$ .

## Thus, the microscopic argument reproduces the same result as the macroscopic argument as required.

If, for a given equilibrium state, there are only a small number of microscopic arrangements possible that will reproduce the macroscopic state then it is extremely unlikely that the macroscopic state will be found as compared with a macroscopic state that can be reproduced by many alternative arrangements of microscopic states. The spontaneous increase in entropy of an isolated system is the change of state from a less probable arrangement to a more probable arrangement.

Since, as the system evolves to a more disordered arrangement the greater the potential number of equivalent microscopic arrangements becomes, we can see that **entropy is greater as the disorder increases** and that therefore **entropy can be viewed as a measure of disorder**. In other words the entropic declaration of the second law

 $\Delta S \ge 0$ 

Implies that

## (i) Disorder has a tendency to increase

and that

(ii) Information tends to be lost.

## Ex.

The specific heat,  $C_P$ , of the alloy  $\beta$ -brass, an alloy of 1:1 Cu:Zn has been measured as a function of temperature. At low temperatures the  $\beta$ -brass crystallizes forming an highly ordered arrangement as it forms a body centre cubic crystal structure;



This abrupt increase in order and therefore reduction in entropy as the temperature is reduced shows itself in a peak in the measured  $C_P$ .

$$\Delta S = \int_{T_1}^{T_2} C_P \frac{dT}{T} \approx 6JK^{-1} \qquad \text{(measured)}$$

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For the ordered crystal each atom has a choice of only  $\frac{N_A}{2}$  sites, as atoms of the other type sit on the others by necessity. If the atom could sit on any of the sites (non-crystalline form of  $\beta$ -Brass) then the choice is of  $2\frac{N_A}{2}$  sites then

$$\Omega_{NonCrystalline} = 2^{N_A} \Omega_{Crystalline}$$

$$\Delta S = k_B \ln \left( 2^{N_A} \Omega \right) - k_B \ln \Omega = N_A k_B \ln 2$$

$$\Delta S = R \ln 2 = 5.76 J K^{-1}$$

So, the increase of specific heat as the sample is heated signals the increase in disorder as the crystalline structure is lost and the consequent increase in entropy.

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## The Carnot Engine Revisited.



Finally, with our new state variable *S* we may gain insight into previously studied systems. For example the Carnot cycle.

Other state variables may be represented on diagrams equivalent to the *P*-*V* diagram and the T - S diagram offers an interesting way to represent the Carnot cycle whose *P*-*V* diagram is shown above.



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On the *T*-*S* diagram the isotherms are represented by the horizontal lines of constant temperature at  $T_1$  and  $T_2$  and during the adiabatic processes no heat is exchanged and  $\Delta S$  is zero, thus the adiabats are represented by the two vertical lines.

The area inside the rectangle representing the Carnot cycle on a T - S diagram is

$$T_{1} \int_{S_{1}}^{S_{2}} dS + T_{2} \int_{S_{2}}^{S_{1}} dS = Q_{1} - Q_{2} = \Delta T \Delta S$$

ie. it is the total heat absorbed. By application of the first law and the fact that over a cycle  $\Delta U$  = 0 the area is also the net work done.

NB. The zero point on the S axis is arbitrary but the origin of the temperature axis is absolute where the thermodynamic temperature scale may be used. Consideration of the *T*-*S* diagram for a Carnot engine also allows us to obtain the Carnot form of the efficiency straight away by simple calculation of areas

$$\eta_E = \frac{W}{Q_1} = \frac{\Delta T \Delta S}{T_1 \Delta S} = \frac{T_1 - T_2}{T_1} = 1 - \frac{T_2}{T_1}$$

As obtained previously for the Carnot engine.

C

## **Appendix**

We can make the argument for the form of  $f(\Omega)$  more formal as follows;

$$f(\Omega_1 \Omega_2) = f(\Omega_1) + f(\Omega_2)$$

and therefore we can hold  $\Omega_2$  constant and take the partial differential of  $f(\Omega_1 \Omega_2)$  wrt  $\Omega_1$ Treating this as a function of a function with  $\Omega_2$  a constant the differentiation yields

$$\frac{\partial f}{\partial \Omega_{1}} = \Omega_{2} f^{\prime} (\Omega_{1} \Omega_{2}) = f^{\prime} (\Omega_{1})$$

And holding  $\Omega_1$  and differentiating wrt  $\Omega_2$  using the product rule on  $\Omega_2 f'(\Omega_1 \Omega_2)$ 

$$\frac{\partial^2 f}{\partial \Omega_2 \partial \Omega_1} = f'(\Omega_1 \Omega_2) + \Omega_1 \Omega_2 f''(\Omega_1 \Omega_2) = 0$$

writing

$$y = \Omega_1 \Omega_2 \implies y f''(y) + f'(y) = 0$$

And thus

$$\frac{f''(y)}{f'(y)} = -\frac{1}{y}$$

Now writing  $g = f^{/}$ 

$$\frac{g'(y)}{g(y)} = \frac{d}{dy} \ln g(y) = -\frac{1}{y}$$

Therefore by integration of the above wrt *y* 

$$ln g(y) = -ln y + C_1$$

Taking exponentials of both sides

$$f'(y) = g(y) = \frac{exp(C_1)}{y} = \frac{C_2}{y}$$

therefore

$$f(y) = C_2 \ln y + C_3$$