

**PH605**

**Thermal and  
Statistical Physics**

**M.J.D.Mallett**

**P.Blümler**

**Recommended text books:**

- Finn C.B.P. : Thermal Physics
- Adkins C.J. : Equilibrium Thermodynamics
- Mandl F: Statistical Physics

THERMODYNAMICS .....	4
<i>Review of Zeroth, First, Second and Third Laws.....</i>	4
Thermodynamics.....	4
The zeroth law of thermodynamics,.....	4
Temperature, T .....	4
Heat, Q .....	4
Work, W.....	4
Internal energy, U .....	5
The first law of thermodynamics, .....	5
Isothermal and Adiabatic Expansion .....	6
Heat Capacity .....	6
Heat capacity at constant volume, $C_V$ .....	7
Heat capacity at constant pressure, $C_P$ .....	7
Relationship between $C_V$ and $C_P$ .....	8
The second law of thermodynamics, .....	8
Heat Engines .....	9
Efficiency of a heat engine .....	10
The Carnot Cycle .....	11
The Otto Cycle .....	13
<i>Concept of Entropy : relation to disorder.....</i>	15
The definition of Entropy.....	16
Entropy related to heat capacity .....	16
The entropy of a rubber band.....	17
The third law of thermodynamics, .....	18
The central equation of thermodynamics.....	18
The entropy of an ideal gas .....	18
<i>Thermodynamic Potentials : internal energy, enthalpy, Helmholtz and Gibbs functions, chemical potential .....</i>	19
Internal energy .....	20
Enthalpy .....	20
Helmholtz free energy.....	20
Gibbs free energy .....	21
Useful work.....	21
Chemical Potential .....	22
The state functions in terms of each other .....	22
<i>Differential relationships : the Maxwell relations.....</i>	23
Maxwell relation from U .....	23
Maxwell relation from H .....	24
Maxwell relation from F .....	24
Maxwell relation from G .....	25
Use of the Maxwell Relations.....	26
<i>Applications to simple systems.....</i>	26
The thermodynamic derivation of Stefan's Law .....	27
<i>Equilibrium conditions : phase changes.....</i>	28
Phase changes .....	28
P-T Diagrams .....	29
PVT Surface.....	29
First-Order phase change .....	30
Second-Order phase change.....	31

Phase change caused by ice skates.....	31
The Clausius-Clayperon Equation for 1 <sup>st</sup> order phase changes. ....	32
The Ehrenfest equation for 2 <sup>nd</sup> order phase changes .....	33
BASIC STATISTICAL CONCEPTS .....	35
<i>Isolated systems and the microcanonical ensemble : the Boltzmann-Planck</i>	
<i>Entropy formula</i> .....	35
Why do we need statistical physics ?.....	35
Macrostates and Microstates.....	35
Classical vs Quantum.....	36
The thermodynamic probability, $\Omega$ .....	36
How many microstates ?.....	36
What is an ensemble ?.....	37
Stirling's Approximation .....	39
<i>Entropy and probability</i> .....	39
The Boltzmann-Planck entropy formula.....	40
Entropy related to probability .....	40
The Schottky defect .....	41
<i>Spin half systems and paramagnetism in solids</i> .....	43
<i>Systems in thermal equilibrium and the canonical ensemble : the Boltzmann distribution</i> .....	45
The Boltzmann distribution .....	45
<i>Single particle partition function, <math>Z</math>, and <math>Z_N</math> for localised particles : relation to Helmholtz function and other thermodynamic parameters</i> .....	47
The single particle partition function, $Z$ .....	47
The partition function for localised particles .....	47
The N-particle partition function for distinguishable particles.....	47
The N-particle partition function for indistinguishable particles.....	48
Helmholtz function .....	49
Adiabatic cooling .....	50
Thermodynamic parameters in terms of $Z$ .....	53

## Thermodynamics

### Review of Zeroth, First, Second and Third Laws

#### Thermodynamics

Why study thermal and statistical physics ? What use is it ?

#### The zeroth law of thermodynamics,

*If each of two systems is in thermal equilibrium with a third, then they are also in thermal equilibrium with each other.*

This implies the existence of a property called temperature. Two systems that are in thermal equilibrium with each other must have the same temperature.

#### Temperature, $T$

The 0<sup>th</sup> law of thermodynamics implies the existence of a property of a system which we shall call temperature,  $T$ .

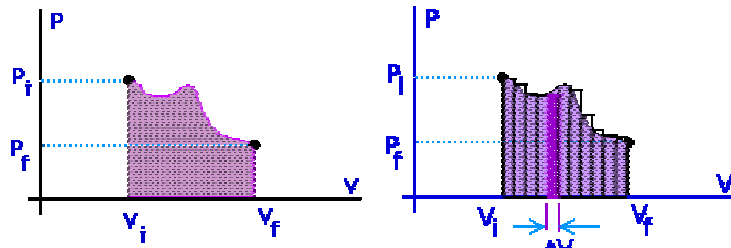
#### Heat, $Q$

In general terms this is an amount of energy that is supplied to or removed from a system. When a system absorbs or rejects heat the state of the system must change to accommodate it. This will lead to a change in one or more of the thermodynamic parameters of the system e.g. the temperature,  $T$ , the volume,  $V$ , the pressure,  $P$ , etc.

#### Work, $W$

When a system has work done on it, or if it does work itself, then there is a flow of energy either into or out of the system. This will also lead to a change in one or more of the thermodynamics parameters of the system in the same way that gaining or losing heat,  $Q$ , will cause a change in the state of the system, so too will a change in the work,  $W$ , done on or by the system.

When dealing with gases, the work done is usually related to a change in the volume,  $dV$ , of the gas. This is particularly apparent in a machine such as a cars engine.



### Internal energy, U

The internal energy of a system is a measure of the total energy of the system. If it were possible we could measure the position and velocity of every particle of the system and calculate the total energy by summing up the individual kinetic and potential energies.

$$U = \sum_{n=1}^N KE + \sum_{n=1}^N PE$$

However, this is not possible, so we are never able to measure the internal energy of a system. What we can do is to measure a change in the internal energy by recording the amount of energy either entering or leaving a system.

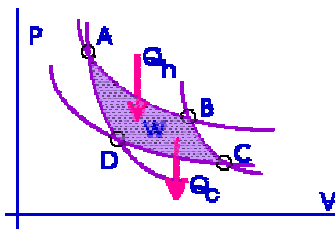
In general, when studying thermodynamics, we are interested in changes of state of a system.

$$\Delta U = \Delta Q + \Delta W$$

which we usually write,

$$dU = \delta Q + \delta W$$

The bar through the differential,  $\delta$ , means that the differential is inexact, this means that the differential is path dependent i.e. the actual value depends on the route taken, not just the start and finish points.



### The first law of thermodynamics,

*If a thermally isolated system is brought from one equilibrium state to another, the work necessary to achieve this change is independent of the process used.*

We can write this as,

$$dU = \delta W_{\text{Adiabatic}}$$

Note : when we consider work done we have to decide on a sign convention. By convention, work done on a system (energy gain by the system) is positive and work done by the system (loss of energy by the system) is negative.

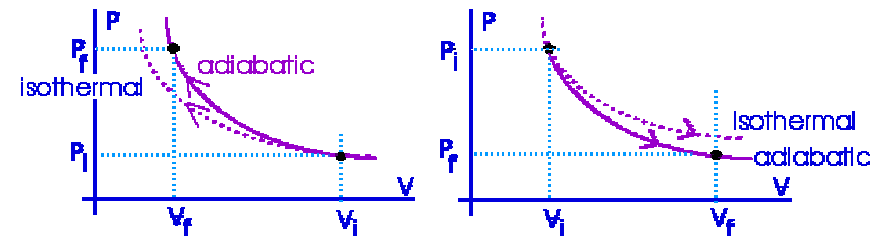
e.g.

- $\delta W = +PdV$  : compression of gas in a pump ( $T$  of gas increases).
- $\delta W = -PdV$  : expansion of gas in an engine ( $T$  of gas decreases).

### Isothermal and Adiabatic Expansion

When we consider a gas expanding, there are two ways in which this can occur, *isothermally* or *adiabatically*.

- **Isothermal expansion** : as it's name implies this is when a gas expands or contracts at a constant temperature ('iso'-same, 'therm'-temperature). This can only occur if heat is absorbed or rejected by the gas, respectively. The final and initial states of the system will be at the same temperature.



- **Adiabatic expansion** : this is what happens when no heat is allowed to enter or leave the system as it expands or contracts. The final and initial states of the system will be at different temperatures.

### Heat Capacity

As a system absorbs heat it changes its state (e.g.  $P, V, T$ ) but different systems behave individually as they absorb the same heat so there must be a parameter governing the heat absorption, this is known as the *heat capacity*,  $C$ .

The heat capacity of a material is defined as the limiting ratio of the heat,  $Q$ , absorbed, to the rise in temperature,  $\Delta T$ , of the material. It is a measure of the amount of heat required to increase the temperature of a system by a given amount.

$$C = \lim_{\Delta T \rightarrow 0} \left( \frac{Q}{\Delta T} \right)$$

When a system absorbs heat its state changes to accommodate the increase of internal energy, therefore we have to consider how the heat capacity of a system is governed when there are restrictions placed upon how the system can change.

In general we consider systems kept at constant volume and constant temperature and investigate the heat capacities for these two cases.

#### Heat capacity at constant volume, $C_V$

If the volume of the system is kept fixed then no work is done and the heat capacity can be written as,

$$C_V = \frac{dQ_V}{dT} = \left( \frac{\partial U}{\partial T} \right)_V$$

#### Heat capacity at constant pressure, $C_P$

The heat capacity at constant pressure is therefore analogously,

$$C_P = \frac{dQ_P}{dT}$$

We now use a new state function known as *enthalpy*,  $H$ , (which we discuss later).

$$H = U + PV$$

$$\Rightarrow dH = dU + PdV + VdP$$

$$dH = dQ + VdP$$

Using this definition we can write,

$$C_P = \frac{dQ_P}{dT} = \left( \frac{\partial H}{\partial T} \right)_P$$

#### Relationship between $C_V$ and $C_P$

The internal energy of a system can be written as,

$$dU = dQ + dW \\ \Rightarrow dQ = dU - PdV$$

Assuming the change of internal energy is a function of volume and temperature,  $U = U(V, T)$ , i.e. we have a constant pressure process, this can be written as,

$$dQ = \left( \frac{\partial U}{\partial V} \right)_T dV + \left( \frac{\partial U}{\partial T} \right)_V dT + PdV$$

which leads to,

$$\Rightarrow C_P = \frac{dQ_P}{dT} = \left( \frac{\partial U}{\partial V} \right)_T \left( \frac{\partial V}{\partial T} \right)_P + \left( \frac{\partial U}{\partial T} \right)_V + P \left( \frac{\partial V}{\partial T} \right)_P \\ \therefore C_P = C_V + \left[ P + \left( \frac{\partial U}{\partial V} \right)_T \right] \left( \frac{\partial V}{\partial T} \right)_P$$

This is the general relationship between  $C_V$  and  $C_P$ .

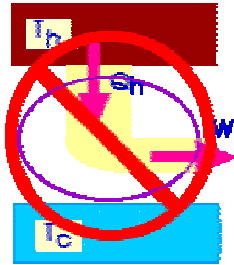
In the case of an ideal gas the internal energy is independent of the volume (there is zero interaction between gas particles), so the formula simplifies to,

$$C_P = C_V + P \left( \frac{\partial V}{\partial T} \right)_P \\ \Rightarrow C_P - C_V = R$$

#### The second law of thermodynamics,

The Kelvin statement of the 2<sup>nd</sup> law can be written as,

*It is impossible to construct a device that, operating in a cycle, will produce no effect other than the extraction of heat from a single body at a uniform temperature and the performance of an equivalent amount of work.*

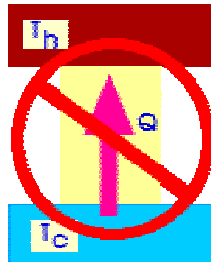


A more concise form of this statement is,

*A process whose only effect is the complete conversion of heat into work is impossible.*

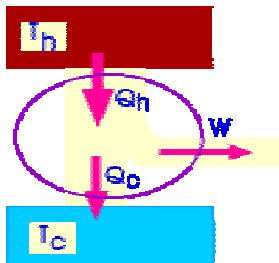
Another form of the 2<sup>nd</sup> law is known as the Clausius statement,

*It is impossible to construct a device that, operating in a cycle, will produce no effect other than the transfer of heat from a colder to a hotter body.*

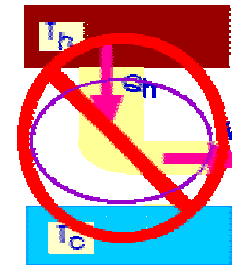


### Heat Engines

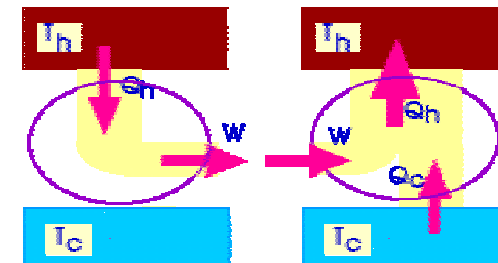
Heat engines convert internal energy to mechanical energy. We can consider taking heat  $Q_H$  from a hot reservoir at temperature  $T_H$  and using it to do useful work  $W$ , whilst discarding heat  $Q_C$  to a cold reservoir  $T_C$ .



It would be useful to convert all the heat,  $Q_H$ , extracted into useful work but this is disallowed by the 2<sup>nd</sup> law of thermodynamics.



If this process were possible it would be possible to join two heat engines together, whose sole effect was the transport of heat from a cold reservoir to a hot reservoir.



### Efficiency of a heat engine

We can define the efficiency of a heat engine as the ratio of the work done to the heat extracted from the hot reservoir.

$$\eta = \frac{W}{Q_H} = \frac{Q_H - Q_C}{Q_H} = 1 - \frac{Q_C}{Q_H}$$

From the definition of the absolute temperature scale<sup>1</sup>, we have the relationship,

$$\frac{Q_C}{T_C} = \frac{Q_H}{T_H}$$

<sup>1</sup> For a proof of this see Finn CP, Thermal Physics,

One way of demonstrating this result is the following. Consider two heat engines which share a common heat reservoir. Engine 1 operates between  $T_1$  and  $T_2$  and engine 2 operates between  $T_2$  and  $T_3$ . We can say that there must be a relationship between the ratio of the heat extracted/absorbed to the temperature difference between the two reservoirs, i.e.

$$\frac{Q_1}{Q_2} = f(\theta_1, \theta_2) \quad , \quad \frac{Q_2}{Q_3} = f'(\theta_2, \theta_3) \quad , \quad \frac{Q_1}{Q_3} = f''(\theta_1, \theta_3)$$

Therefore the overall heat engine can be considered as a combination of the two individual engines.

$$f''(\theta_1, \theta_3) = f(\theta_1, \theta_2) f'(\theta_2, \theta_3)$$

However this can only be true if the functions factorize as,

$$f(\theta_x, \theta_y) \rightarrow \frac{T(\theta_x)}{T(\theta_y)}$$

Where  $T(\theta)$  represents a function of absolute, or thermodynamic temperature. Therefore we have the relationship,

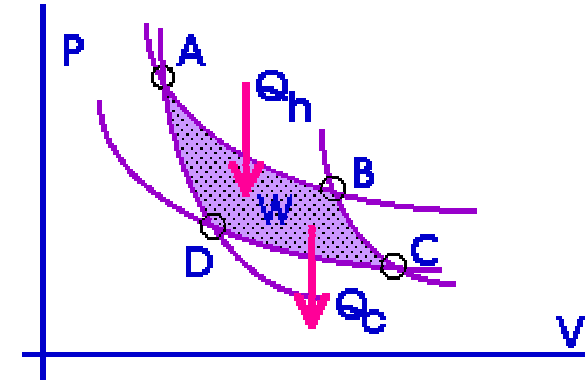
$$\frac{Q_1}{Q_2} = \frac{T(\theta_1)}{T(\theta_2)}$$

Therefore we can also write the efficiency relation as,

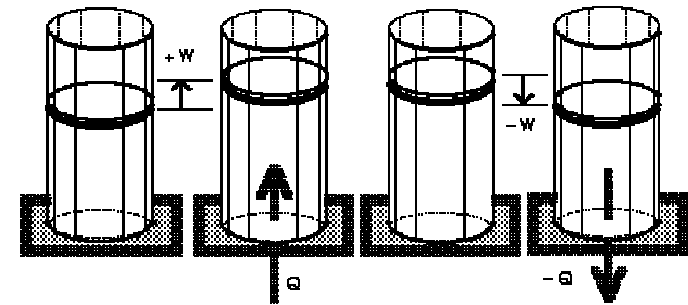
$$\eta = 1 - \frac{T_C}{T_H}$$

The efficiency of a reversible heat engine depends upon the temperatures between which it operates. The efficiency is always  $< 1$ . The most efficient heat engine is typified by the Carnot cycle.

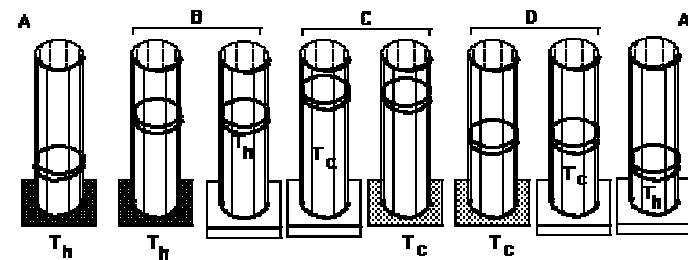
### The Carnot Cycle



The Carnot cycle is a closed cycle which extracts heat  $Q_H$  from a hot reservoir and discards heat  $Q_C$  into a cold reservoir while doing useful work,  $W$ . The cycle operates around the cycle  $A \rightarrow B \rightarrow C \rightarrow D \rightarrow A$ .

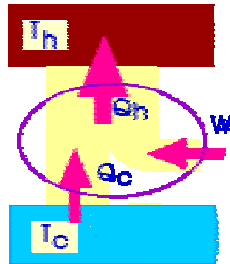


We can consider this cycle in terms of the expansion/contraction of an ideal gas.



A heat engine can also operate in reverse, extracting heat,  $Q_C$  from a cold reservoir and discarding heat,  $Q_H$ , into a hot reservoir by having work done on it,  $W$ , the total heat discarded into the hot reservoir is then,

$$Q_H = Q_C + W$$



This is the principle of the refrigerator.

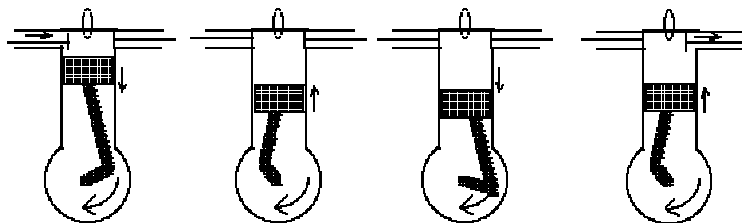
### The Otto Cycle

The Carnot cycle represents the most efficient heat engine that we can contrive. In reality it is unachievable.

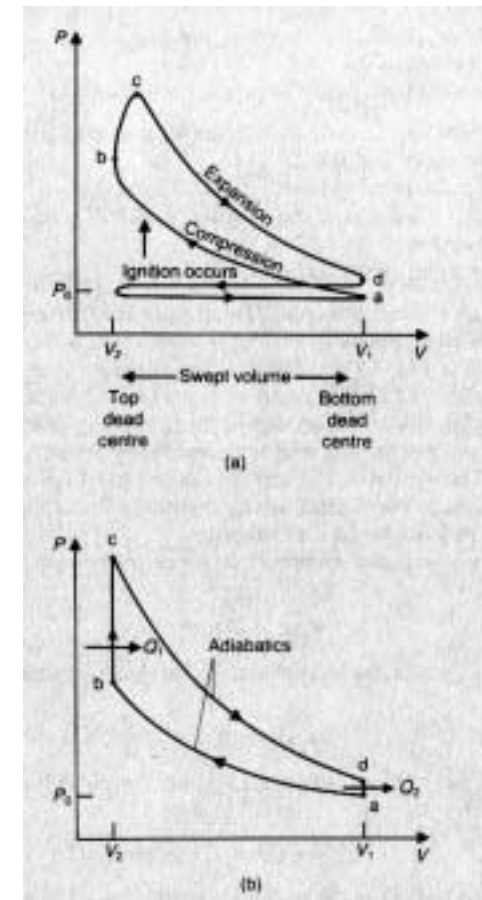
Two of the most common heat engines are found in vehicles, the 4-stroke petrol engine and the 4-stroke diesel engine.

The 4-stroke cycle can be considered as:

1. Induction : Petrol/Air mixture drawn into the engine cylinder.
2. Compression : Petrol/Air mixture compressed to a small volume by the rising piston.
3. Power : Ignition of petrol/air mixture causes rapid expansion pushing the piston down the cylinder
4. Exhaust : Exhaust gases evacuated from the cylinder by the rising piston.

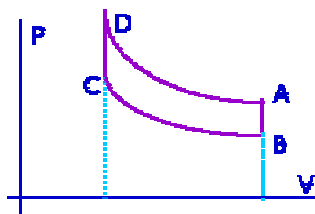
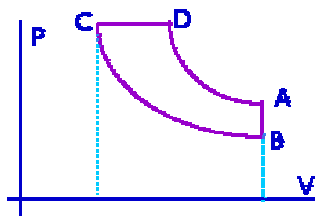


The 4-stroke petrol engine follows the Otto cycle rather than the Carnot cycle. The actual cycle differs slightly from the idealised cycle to accommodate the introduction of fresh petrol/air mixture and the evacuation of exhaust gases.



The Otto cycle and the Diesel cycle can be approximated by PV diagrams.

### Otto cycle

**Diesel cycle****Concept of Entropy : relation to disorder**

We shall deal with the concept of entropy from both the thermodynamic and the statistical mechanical aspects.

Suppose we have a reversible heat engine that absorbs heat  $Q_1$  from a hot reservoir at a temperature  $T_1$  and discards heat  $Q_2$  into a cold reservoir at a temperature  $T_2$ , then from the efficiency relation we have,

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

but from the 2<sup>nd</sup> law we know that we cannot have a true reversible cycle, there is always a heat loss, therefore we should rewrite this relationship as,

$$\frac{Q_1}{T_1} < \frac{Q_2}{T_2}$$

The heat absorbed in one complete cycle of the heat engine is therefore,

$$\oint \frac{dQ}{T} \leq 0$$

This is known as the Clausius inequality.

If we had a truly reversible heat engine then this would be,

$$\oint_R \frac{dQ}{T} = 0$$

The inequality of an irreversible process is a measure of the change of entropy of the process.

$$\Delta S = S_{final} - S_{initial} = \int_{initial}^{final} \frac{dQ}{T}$$

so for an infinitesimal part of the process we have,

$$dS \geq \frac{dQ}{T}$$

**The definition of Entropy**

An entropy change in a system is defined as,

$$dS = \frac{dQ}{T}$$

*The entropy of a thermally isolated system increases in any irreversible process and is unaltered in a reversible process. This is the principle increasing entropy.*

The entropy of a system can be thought of as the inevitable loss of precision, or order, going from one state to another. This has implications about the direction of time.

The forward direction of time is that in which entropy increases – so we can always deduce whether time is evolving backwards or forwards.

Although entropy in the Universe as a whole is increasing, on a local scale it can be decreased – that is we can produce systems that are more precise – or more ordered than those that produced them. An example of this is creating a crystalline solid from amorphous components. The crystal is more ordered and so has lower entropy than its precursors.

On a larger scale – life itself is an example of the reduction of entropy. Living organisms are more complex and more ordered than their constituent atoms.

**Entropy related to heat capacity**

Suppose the heat capacity of a solid is  $C_P = 125.48 \text{ J K}^{-1}$ . What would be the entropy change if the solid is heated from 273 K to 373 K ?

Knowing the heat capacity of the solid and the rise in temperature we can easily calculate the heat input and therefore the entropy change.

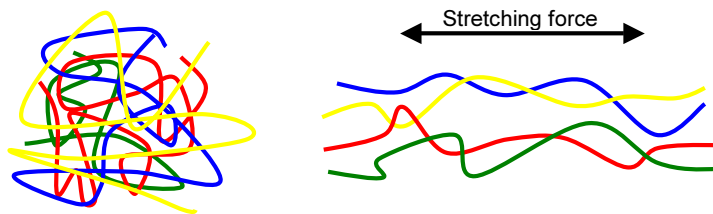
$$dS = \frac{dQ}{T}$$

We integrate over the temperature range to determine the total entropy change.

$$\begin{aligned}\Delta S &= S_{final} - S_{initial} = \int_{T_{initial}}^{T_{final}} \frac{dQ}{T} \\ &= \int_{T_{initial}}^{T_{final}} \frac{C_p dT}{T} \\ &= C_p \ln \left( \frac{T_{final}}{T_{initial}} \right) = 39.2 \text{ JK}^{-1}\end{aligned}$$

### The entropy of a rubber band

A rubber band is a collection of long chain polymer molecules. In its relaxed state the polymers are highly disordered and entangled. The amount of disorder is high and so the entropy of the system must be high.



If the rubber band is stretched then the polymers become less entangled and align with the stretching force. They form a quasi-crystalline state. This is a more ordered state and must therefore have a lower entropy.

The total entropy in the stretched state is made up of spatial and thermal terms.

$$S_{Total} = S_{Spatial} + S_{Thermal}$$

If the tension in the band is rapidly reduced then we are performing an adiabatic (no heat flow) change on the system. The total entropy must remain unchanged since there is no heat flow, but the spatial entropy has increased so the thermal entropy must decrease. This means the temperature of the rubber band drops.

### The third law of thermodynamics,

*The entropy change in a process, between a pair of equilibrium states, associated with a change in the external parameters tends to zero as the temperature approaches absolute zero.*

Or more succinctly,

*The entropy of a closed system always increases.*

An alternative form of the 3<sup>rd</sup> law given by Planck is,

*The entropy of all perfect crystals is the same at absolute zero and may be taken as zero.*

In essence this is saying that at absolute zero there is only one possible state for the system to exist in so there is no ambiguity about the possibility of it existing in one of several different states.

This concept becomes more evident when we consider the statistical concept of entropy.

### The central equation of thermodynamics

The differential form of the first law of thermodynamics is,

$$dU = \delta Q + \delta W$$

Using our definition for entropy and assuming we are dealing with a compressible fluid we can write this as,

$$dU = TdS - PdV$$

This is more usually written as,

$$TdS = dU + PdV$$

This assumes that all the work done is due to changes of pressure, rather than changes of magnetisation etc.

### The entropy of an ideal gas

The specific heat capacity at constant volume for a gas is,

$$C_V = \left( \frac{\partial U}{\partial T} \right)_V = \frac{dU}{dT}$$

Substituting this into the central equation gives,

$$TdS = C_V dT + PdV$$

If we consider one mole of an ideal gas and use lower case letters to refer to molar quantities then we can write this as,

$$Tds = c_v dT + \frac{RT}{v} dv$$

$$ds = c_v \frac{dT}{T} + R \frac{dv}{v}$$

Integrating both sides gives us,

$$s = c_v \ln T + R \ln v + s_0$$

So the entropy of an ideal gas has three main terms,

1. A temperature term – related to the motion, and therefore kinetic energy of the gas
2. A volume term – related to the positions of the gas particles
3. A constant term – the intrinsic disorder term which is un-measurable.

As an example of this can be used, consider gas inside a cylinder of volume,  $V_0$ . Suppose the volume of the cylinder is suddenly doubled. What is the increase in entropy of the gas ?

Assuming this change occurs at constant temperature, we can write,

$$\Delta s = s_{2V_0} - s_{V_0} = R \ln 2V_0 - R \ln V_0$$

$$= R \ln \left( \frac{2V_0}{V_0} \right) = R \ln 2$$

If we were dealing with more than one mole of gas we could write this as,

$$\Delta s = nR \ln 2$$

$$= Nk_B \ln 2$$

Where  $n$  is the number of moles and  $N$  is the number of molecules. We will return to this result when we look at the statistical definition of entropy.

**Thermodynamic Potentials : internal energy, enthalpy, Helmholtz and Gibbs functions, chemical potential**

The equilibrium conditions of a system are governed by the thermodynamic potential functions. These potential functions tell us how the state of the system will vary, given specific constraints.

The differential forms of the potentials are exact because we are now dealing with the state of the system.

### Internal energy

This is the total internal energy of a system and can be considered to be the sum of the kinetic and potential energies of all the constituent parts of the system.

$$U = \sum_{n=1}^{\infty} KE + \sum_{n=1}^{\infty} PE$$

This quantity is poorly defined since we are unable to measure the individual contributions of all the constituent parts of the system.

Using this definition of internal energy and the 2<sup>nd</sup> law of thermodynamics we are able to combine the two together to give us one of the central equations of thermodynamics,

$$TdS = dU + PdV$$

This enables us to calculate changes to the internal energy of a system when it undergoes a change of state.

$$dU = TdS - PdV$$

### Enthalpy

This is sometimes erroneously called the *heat content* of a system. This is a state function and is defined as,

$$H = U + PV$$

We are more interested in the change of enthalpy,  $dH$ , which is a measure of the heat of reaction when a system changes state. In a mechanical system this could be when we have a change in pressure or volume. In a predominantly chemical system this could be due to the heat of reaction of a change in the chemistry of the system.

$$dH = dU + PdV + VdP$$

### Helmholtz free energy

The Helmholtz free energy of a system is the maximum amount of work obtainable in which there is no change in temperature. This is a state function and is defined as,

$$F = U - TS$$

The change of Helmholtz free energy is given by,

$$\begin{aligned} dF &= dU - TdS - SdT \\ &= -PdV - SdT \end{aligned}$$

### Gibbs free energy

The Gibbs free energy of a system is the maximum amount of work obtainable in which there is no change in volume. This is a state function and is defined as,

$$G = H - TS$$

The change of Gibbs free energy is given by,

$$\begin{aligned} dG &= dH - TdS - SdT \\ &= VdP - SdT \end{aligned}$$

It is obvious that the Helmholtz and Gibbs free energies are related,

$$\Delta G = \Delta F + \Delta(PV)$$

and the correct one to use has to be ascertained for the system in hand. For example, a metal undergoes very small volume changes so we could use the Gibbs function whereas a gas usually has large volume changes associated with it and we have to choose the function depending upon the situation.

### Useful work

Suppose we have a system that does work and that part of that work involves a volume change. If the system returns to its initial state of pressure and temperature at the end of it doing some work then there is no temperature change, i.e.

- Initial temperature and pressure =  $T_0$  and  $P_0$
- Final temperature and pressure =  $T_0$  and  $P_0$

Then because there is no overall temperature change, the maximum amount of work done by the system is given by the decrease in the Helmholtz free energy,  $F$ , of the system.

$$W_{Total} = -\Delta F$$

However, some of the work done is useless work, suppose the actual gas expansion was a by product of some chemical reaction, then we would want to know how much useful work has actually been done.

$$\begin{aligned} W_{Useful} &= W_{Total} - W_{Useless} \\ &= W_{Total} - P_0 \Delta V \\ &= -\Delta F - P_0 \Delta V \\ &= -\Delta(F + P_0 V) \\ W_{Useful} &= -\Delta G \end{aligned}$$

Therefore, the decrease in the Gibbs free energy tells us how much useful work was done by this process.

### Chemical Potential

This is important when the quantity of matter is not fixed (e.g. we are dealing with a changing number of atoms within a system). When this happens we have to modify our thermodynamic relations to take account of this.

$$\begin{aligned} dU &= TdS - PdV + \mu dN \\ dF &= -PdV - SdT + \mu dN \\ dG &= VdP - SdT + \mu dN \end{aligned}$$

This means that there are several ways of writing the chemical potential,  $\mu$ .

$$\mu = \left( \frac{\partial U}{\partial N} \right)_{S,V} = \left( \frac{\partial F}{\partial N} \right)_{V,T} = \left( \frac{\partial G}{\partial N} \right)_{T,P}$$

We can also show that the chemical potential can be written,

$$\mu = \frac{G}{N}$$

*The chemical potential,  $\mu$ , is the Gibbs free energy per particle, provided only one type of particle is present.*

### The state functions in terms of each other

We can write infinitesimal state functions for the internal energy,  $U$ , the enthalpy,  $H$ , the Helmholtz free energy,  $F$  and the Gibbs free energy,  $G$ .

$$\begin{aligned} dU &= TdS - PdV \\ dH &= TdS + VdP \\ dF &= -SdT - PdV \end{aligned}$$

$$dG = -SdT + VdP$$

By inspection of these equations it would appear that there are natural variables which govern each of the state functions.

For instance, from the formula for the Helmholtz free energy we can assume its natural variables are temperature and volume and therefore we can write,

$$\left(\frac{\partial F}{\partial T}\right)_V = -S \quad \text{and} \quad \left(\frac{\partial F}{\partial V}\right)_T = -P$$

and from the formula for the Gibbs free energy, assuming its natural variables are temperature and pressure, we have,

$$\left(\frac{\partial G}{\partial T}\right)_P = -S \quad \text{and} \quad \left(\frac{\partial G}{\partial P}\right)_T = V$$

This means that if we know one of the thermodynamic potentials in terms of its natural variables then we can calculate the other state functions from it.

Suppose we know the Gibbs free energy,  $G$ , in terms of its natural variables  $T$  and  $P$ , then we can write,

$$U = G - PV + TS = G - P\left(\frac{\partial G}{\partial P}\right)_T - T\left(\frac{\partial G}{\partial T}\right)_P$$

$$H = G + TS = G - T\left(\frac{\partial G}{\partial T}\right)_P$$

$$F = G - PV = G - P\left(\frac{\partial G}{\partial P}\right)_T$$

### Differential relationships : the Maxwell relations

The Maxwell relations are a series of equations which we can derive from the equations of state for  $U$ ,  $H$ ,  $F$  and  $G$ .

#### Maxwell relation from $U$

We already have an equation of state for  $dU$ ,

$$dU = TdS - PdV$$

This suggests that  $U$  is a function of  $S$  and  $V$ , therefore we could rewrite this as,

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

which would then mean that we can write,

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

moreover we can then write,

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

This is the first Maxwell relation.

#### Maxwell relation from $H$

We already have an equation of state for  $dH$ ,

$$dH = TdS + VdP$$

This suggests that  $H$  is a function of  $S$  and  $P$ , therefore we could rewrite this as,

$$dH = \left(\frac{\partial H}{\partial S}\right)_P dS + \left(\frac{\partial H}{\partial P}\right)_S dP$$

which would then mean that we can write,

$$T = \left(\frac{\partial H}{\partial S}\right)_P \quad \text{and} \quad V = \left(\frac{\partial H}{\partial P}\right)_S$$

moreover we can then write,

$$\left(\frac{\partial V}{\partial S}\right)_P = \left(\frac{\partial T}{\partial P}\right)_S$$

This is the second Maxwell relation.

#### Maxwell relation from $F$

We already have an equation of state for  $dF$ ,

$$dF = -SdT - PdV$$

This suggests that  $F$  is a function of  $T$  and  $V$ , therefore we could rewrite this as,

$$dF = \left(\frac{\partial F}{\partial T}\right)_V dT + \left(\frac{\partial F}{\partial V}\right)_T dV$$

which would then mean that we can write,

$$S = -\left(\frac{\partial F}{\partial T}\right)_V \quad \text{and} \quad P = -\left(\frac{\partial F}{\partial V}\right)_T$$

moreover we can then write,

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

This is the third Maxwell relation.

### Maxwell relation from G

We already have an equation of state for  $dG$ ,

$$dG = VdP - SdT$$

This suggests that  $G$  is a function of  $P$  and  $T$ , therefore we could rewrite this as,

$$dG = \left(\frac{\partial G}{\partial P}\right)_T dP + \left(\frac{\partial G}{\partial T}\right)_P dT$$

which would then mean that we can write,

$$V = \left(\frac{\partial G}{\partial P}\right)_T \quad \text{and} \quad S = -\left(\frac{\partial G}{\partial T}\right)_P$$

moreover we can then write,

$$\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T$$

This is the fourth Maxwell relation.

### Use of the Maxwell Relations

Consider applying pressure to a solid (very small volume change), reversibly and isothermally. The pressure applied changes from  $P_1$  to  $P_2$  at a temperature,  $T$ . The process is reversible so we can write,

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

Since the only variables we have are pressure,  $P$  and temperature,  $T$ , we can write the entropy change of the system as a function of these two variables.

$$dS = \left(\frac{\partial S}{\partial P}\right)_T dP + \left(\frac{\partial S}{\partial T}\right)_P dT$$

so therefore,

$$dQ_R = TdS = T\left(\frac{\partial S}{\partial P}\right)_T dP$$

The second term is zero since the process is isothermal,  $dT=0$ .

Using the Maxwell relation derived from the Gibbs free energy,

$$\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T$$

we can then write,

$$dQ_R = -T\left(\frac{\partial V}{\partial T}\right)_P dP = -TV\beta dP$$

Where  $\beta$  is the coefficient of expansion. Integrating this gives,

$$Q = -\int_{P_1}^{P_2} TV\beta dP \\ \approx -TV\beta(P_2 - P_1)$$

The approximation sign assumes  $\beta$  to be constant.

### Applications to simple systems

### The thermodynamic derivation of Stefan's Law

The energy density of thermal radiation (black-body radiation) is dependent only on the temperature of the black body. The energy density at a particular wavelength is then,

$$u_{\lambda} = u_{\lambda}(\lambda, T)$$

and the total energy density is,

$$u = u(T)$$

The Planck formula for the spectral energy density is given by,

$$u_{\lambda}(\lambda, T) = \frac{\beta}{\lambda^5} \left( \frac{1}{e^{\frac{hc}{\lambda k_B T}} - 1} \right)$$

where  $\beta$  is a constant.

The perfect gas theory tells us that the pressure of a gas can be expressed in terms of the mean velocity,  $c$ ,

$$P = \frac{1}{3} \rho c^2$$

but when we are dealing with thermal radiation we can use the Einstein mass-energy relation,

$$E = mc^2 \Rightarrow u = \rho c^2$$

therefore,

$$P = \frac{u}{3}$$

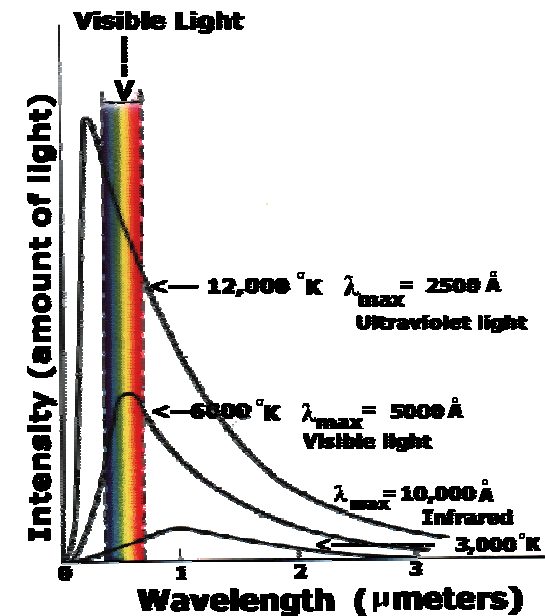
The energy equation for a  $PVT$  system is,

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

substituting into this we have,

$$\begin{aligned} u &= \frac{1}{3} T \frac{du}{dT} - \frac{1}{3} u \\ \frac{4}{3} u &= \frac{T}{3} \frac{du}{dT} \\ 4 \frac{dT}{T} &= \frac{du}{u} \\ \Rightarrow u &= AT^4 \end{aligned}$$

where  $A$  is a constant.



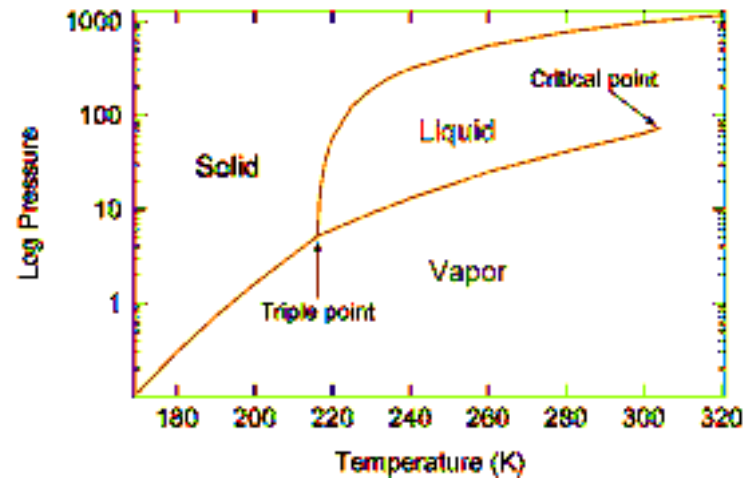
### Equilibrium conditions : phase changes

#### Phase changes

A change of phase of a system occurs when the system changes from one distinct state into another. This change of phase can be caused by many different factors e.g. temperature changes can cause a phase change between a solid and a liquid, applied magnetic fields can cause a phase change between a superconductor and a normal conductor.

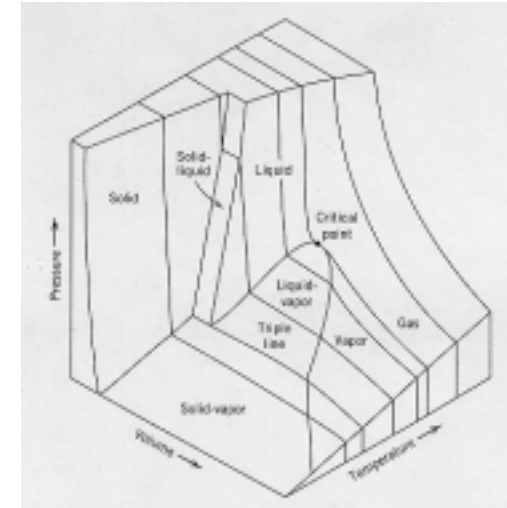
### P-T Diagrams

In a simple system comprising a single substance we can construct a Pressure-Temperature diagram (P-T diagram) showing how changes in pressure or temperature can affect the phase of the system.

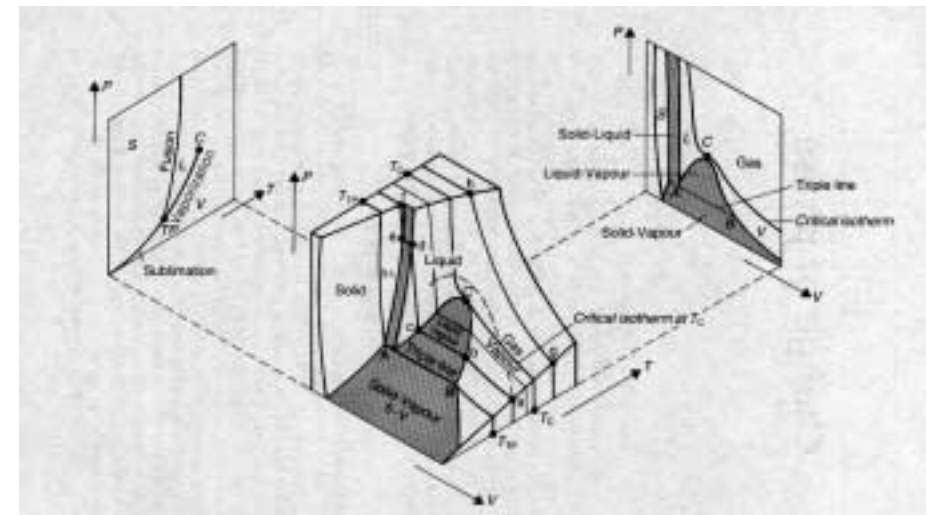


### PVT Surface

The PT diagram is a specialised case of the more general PVT surface. This gives us all the thermodynamic information we require when determining the available phase changes.



Both the PT and PV diagrams can be obtained from the PVT surface by projection.



### First-Order phase change

*A first-order phase change of a substance is characterised by a change in the specific volume between the two phase, accompanied by a latent heat.*

Some typical examples of first-order phase changes are:

- The transition of a solid melting into a liquid.
- The transition of a liquid boiling into a gas.
- The change from superconductor to normal conductor, provided the change occurs in an applied magnetic field.

### Second-Order phase change

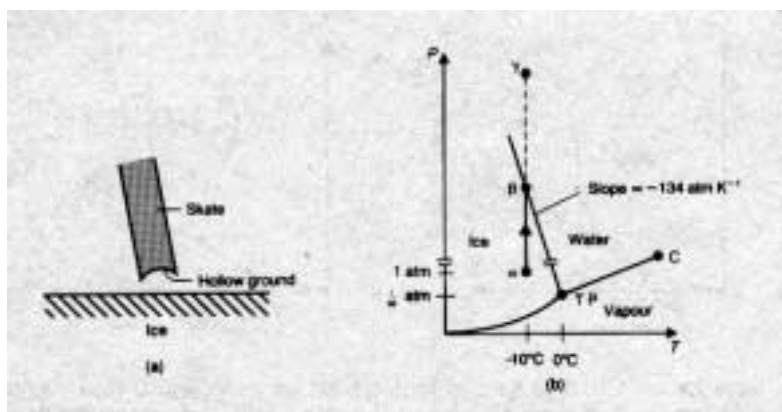
*Second-Order phase change of a substance is characterised by no change in the specific volume between the two phases and no accompanying latent heat.*

Some typical examples of a second-order phase change are:

- The transition from ferro-magnet to para-magnet at the Curie temperature.
- The transition from superconductor to normal conductor, provided there is no applied magnetic field.
- The change from normal liquid  $^4\text{He}$  to superfluid liquid  $^4\text{He}$  below 2.2K

### Phase change caused by ice skates

Water has a particularly interesting phase diagram. It is one the few materials that expands on freezing (or contracts on melting), this is a consequence of the effects of Hydrogen-bonding within the material.



This has implications which can be used to our advantage to allow ice skating. The 'hollow-ground' edge of an ice skate causes an enormous pressure on the ice surface of 100 atmospheres or more. This pressure increase occurs

at constant temperature and the phase of the ice crosses the melting line on the PT diagram. The skater is now standing on a thin layer of water which acts as a lubricant between the skate and the bulk of the ice.

If the temperature is too low then the increased pressure of the skate on the ice surface is insufficient to cause the ice to cross the melting line and so ice skating is not possible.

Skiing is not a pressure-melting effect since the surface area of the sky is far too large to cause melting of snow, instead the effect is caused by frictional heating and wax lubricant applied to the ski.

### The Clausius-Clayperon Equation for 1<sup>st</sup> order phase changes.

When a phase change occurs we are mostly interested in how it affects the Gibbs free energy. At thermodynamic equilibrium the Gibbs function is at a minimum, so at the transition line on the PT diagram the specific Gibbs energy is the same for both phases.

$$g_1(P, T) = g_2(P, T)$$

Further along the transition line we must also have the same condition.

$$g_1(P + dP, T + dT) = g_2(P + dP, T + dT)$$

Expanding this to first order using a Taylor approximation,

$$g_1(P, T) + \left(\frac{\partial g_1}{\partial T}\right)_P dT + \left(\frac{\partial g_1}{\partial P}\right)_T dP = g_2(P, T) + \left(\frac{\partial g_2}{\partial T}\right)_P dT + \left(\frac{\partial g_2}{\partial P}\right)_T dP$$

So therefore,

$$\left[\left(\frac{\partial g_1}{\partial T}\right)_P - \left(\frac{\partial g_2}{\partial T}\right)_P\right] dT = \left[\left(\frac{\partial g_2}{\partial P}\right)_T - \left(\frac{\partial g_1}{\partial P}\right)_T\right] dP$$

From our previous discussion about the natural variables for the Gibbs function, we can write,

$$V = \left(\frac{\partial G}{\partial P}\right)_T \quad \text{and} \quad S = -\left(\frac{\partial G}{\partial T}\right)_P$$

and therefore considering the specific quantities, we have

$$\frac{dP}{dT} = \frac{s_2 - s_1}{v_2 - v_1} = \frac{S_2 - S_1}{V_2 - V_1}$$

The latent heat associated with this phase change is related to the entropy change,

$$L = \Delta Q = T(S_2 - S_1)$$

Which gives us the Clausius-Clayperon equation which is the gradient of the phase transition line for a first order phase change.

$$\frac{dP}{dT} = \frac{L}{T(V_2 - V_1)}$$

### The Ehrenfest equation for 2<sup>nd</sup> order phase changes

In a second order phase change there is no latent heat, and so no entropy change, and no volume change. So using a similar argument as the one for the Clausius-Clayperon equation,

$$s_1(P, T) = s_2(P, T)$$

Further along the transition line we must also have the same condition.

$$s_1(P + dP, T + dT) = s_2(P + dP, T + dT)$$

Expanding this to first order using a Taylor approximation,

$$s_1(P, T) + \left(\frac{\partial s_1}{\partial T}\right)_P dT + \left(\frac{\partial s_1}{\partial P}\right)_T dP = s_2(P, T) + \left(\frac{\partial s_2}{\partial T}\right)_P dT + \left(\frac{\partial s_2}{\partial P}\right)_T dP$$

Now substituting in expressions for the specific heat capacity and the volume expansion,

$$c = T \left(\frac{\partial s}{\partial T}\right)_P \quad \text{and} \quad \beta = \frac{1}{v} \left(\frac{\partial v}{\partial T}\right)_P$$

we can write,

$$\frac{dP}{dT} = \frac{C_{P1} - C_{P2}}{TV(\beta_1 - \beta_2)}$$

This is the first Ehrenfest equation for a 2<sup>nd</sup> order phase change, the second Ehrenfest equation can be derived by considering the continuity of the volume of the two phases, which gives,

$$\frac{dP}{dT} = \frac{\beta_2 - \beta_1}{\kappa_2 - \kappa_1}$$

where  $\kappa$  is the bulk modulus of the phase.

### Basic statistical concepts

#### Isolated systems and the microcanonical ensemble : the Boltzmann-Planck Entropy formula

##### Why do we need statistical physics ?

There are two ways that we can look at the behaviour of matter

1. Mechanical viewpoint : measuring the positions and velocities of atoms at the microscopic level.
2. Thermodynamic viewpoint : measuring the bulk properties of matter at the macroscopic level.

However, when we try and reconcile the two viewpoints we run into a problem. Theoretically we should get the same answers from both viewpoints. However there is a problem with the direction of time,

- Microscopic time : reversible e.g. the laws of motion look identical whichever way time goes.
- Macroscopic time : non-reversible, there is a preferred direction of time defined by the increase of entropy of the Universe.

The two viewpoints can be reconciled by looking at systems from a statistical or probabilistic viewpoint.

##### Macrostates and Microstates

When we are dealing with a system, e.g. a gas inside a container, we can determine various properties of the system. In our example of a gas we can determine, i.e. measure, the volume,  $V$ , the pressure,  $P$ , the temperature,  $T$ , the molecular density,  $\rho$ , plus others.

The state of the system can therefore be defined by quantities such as  $V, P, T$  &  $\rho$ . This is called a *macrostate*. In thermodynamic terms we usually only consider *macrostates*.

However, this gives us no knowledge of the properties of the individual gas particles, for instance their positions or velocities. There are several, effectively infinitely many, states of a system which all have the same *macrostate*. Each of these individual states are known as *microstates*. They have different positions, velocities etc. for the individual particles but all have the same thermodynamic properties such as volume, pressure and temperature.

### Classical vs Quantum

The classical view of the universe allows us an infinite choice of position and velocity. This implies that for any given *macrostate* there must be an infinite number of *microstates* that correspond to it.

The quantum viewpoint however tells us that at the atomic level we are able to assign quantum numbers to the properties of particles. So for a closed system there are only a finite number of states that the system can occupy.

In this scenario the most probable *macrostate* for a system is the one that has the most *microstates* – simply because we have the greatest chance of finding the system in that *microstate*.

##### The thermodynamic probability, $\Omega$

The number of possible microstates for a given macrostate is called the thermodynamic probability,  $\Omega$ , or sometimes,  $W$ . This is not a probability in the normal sense since it has a value greater than or equal to one.

Consider a system of two particles  $A$  and  $B$  that can both exist in one of two energy levels,  $E_1$  and  $E_2$ . The *macrostate* of this system can be defined by the total energy of the system.

Macrostate	(1) $E_1 + E_1$	(2) $E_1 + E_2$	(3) $E_2 + E_2$
Microstate	$A(E_1), B(E_1)$	$A(E_1), B(E_2)$ $A(E_2), B(E_1)$	$A(E_2), B(E_2)$
$\Omega$	1	2	1

Therefore if both energy levels,  $E_1$  and  $E_2$  are equally likely the system has a 50% chance of being in *macrostate* (2) and a 25% chance each of being in *macrostates* (1) and (3).

However, in general not every energy level is equally likely so the most likely *macrostate* is also governed by the probability of energy level occupation.

This leads on to the concept of the partition function,  $Z$ , for a system, which we will cover later.

##### How many microstates ?

Suppose we are dealing with a paramagnetic solid. This means we have atoms arranged in a regular crystalline lattice and each atom acts as a magnetic dipole because it has an unpaired electron.

In a magnetic field the magnetic dipole can either point along the field or against the field. Therefore there are two possible states for each dipole, 'spin-up' or 'spin-down'.

Therefore, for  $N$  atoms ( $N \sim 10^{23}$ ) there must be  $2^N$  possible microstates for the magnetic dipoles.

How long would it take for the system to sample all the possible microstates ?

Assuming a dipole changes orientation every  $10^{-10}$  seconds there would be a new microstate generated every  $10^{-33}$  seconds, so every microstate would be sampled after

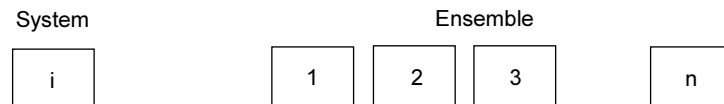
$$\sim 10^{(2^{23} - 33)} \text{ seconds}$$

The lifetime of the Universe is only  $\sim 10^{17}$  seconds !

Instead of considering one system and watching it change we use the concept of an *ensemble*.

### What is an ensemble ?

An ensemble is a very large number of replica systems with identical specifications e.g. volume, temperature, chemistry, number of particles etc. The ensemble represents the *macrostate* of the system while each individual replica represents one of the possible *microstates*.



There are several different ensembles that we might encounter. The type of ensemble is governed by the measurable parameters.

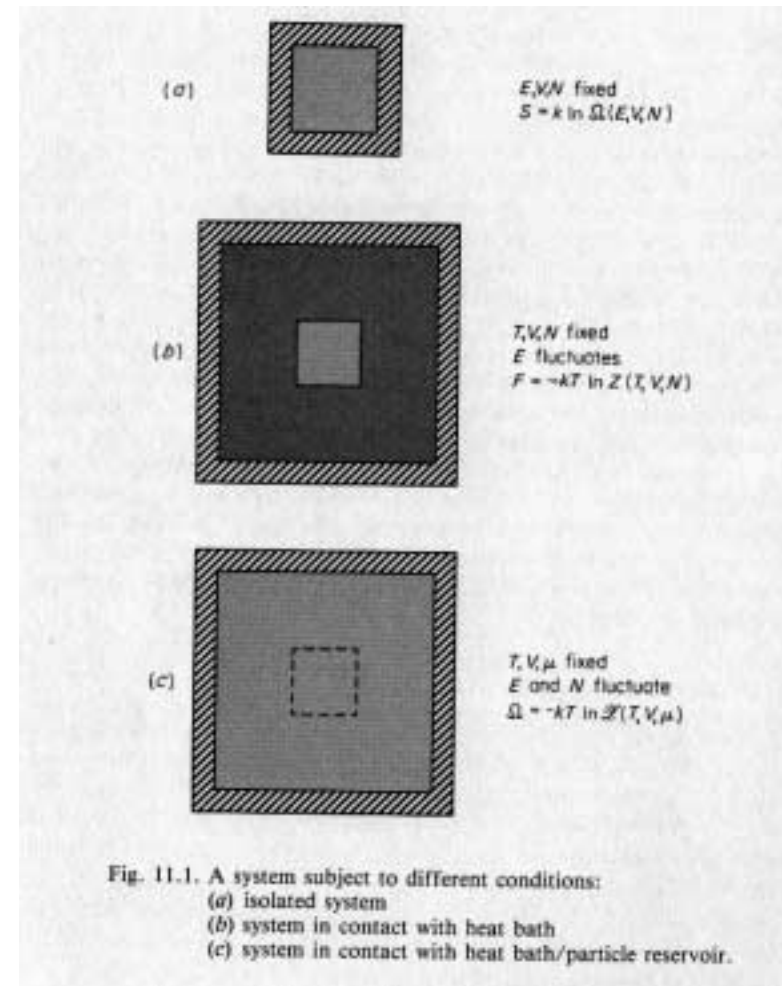


Fig. 11.1. A system subject to different conditions:  
 (a) isolated system  
 (b) system in contact with heat bath  
 (c) system in contact with heat bath/particle reservoir.

1. **Micro-canonical ensemble** : isolated systems, the total internal energy,  $U$ , and number of particles,  $N$ , is well defined.
2. **Canonical ensemble** : systems in thermal equilibrium, the temperature,  $T$ , and number of particles,  $N$ , is well defined.
3. **Grand canonical ensemble** : systems in thermal and chemical contact, the temperature,  $T$ , and chemical potential,  $\mu$ , is well defined.

### Stirling's Approximation

We are now dealing with very large numbers ! Almost any macroscopic system will have on the order of  $10^{23}$  particles.

The mathematics of such large numbers can become very involved but fortunately there are some simple approximations that work well when the  $N$  is very large.

There are two particularly useful approximations known as Stirling's two-term and three-term approximations; they are,

- Stirling's 2-term approximation

$$\ln(N!) = N \ln N - N$$

Example

$$\begin{aligned}\ln(100!) &\approx 100 \ln 100 - 100 \\ &\approx 360.5170 \text{ (Stirlings approximation)} \\ &= 360.7394 \text{ (Actual value)}\end{aligned}$$

- Stirling's 3-term approximation

$$\ln(N!) = N \ln N - N + \ln \sqrt{2\pi N}$$

Example

$$\begin{aligned}\ln(100!) &\approx 100 \ln 100 - 100 + \ln \sqrt{200\pi} \\ &\approx 360.7385 \text{ (Stirlings approximation)} \\ &= 360.7394 \text{ (Actual value)}\end{aligned}$$

These approximations are particularly useful when dealing with thermodynamic probabilities.

### Entropy and probability

In statistical mechanics each particle is seen as having its own dynamic state, a position in space, and a spatial velocity or momentum. In three-dimensional space this gives the particle 3 degrees of freedom.

Three position coordinates and three momentum coordinates place each particle somewhere in the six-dimensional phase space. If there is more than one particle you can consider the system of those particles as having 6 times  $N$  coordinates and hence a single position in a  $6N$ -dimensional phase space.

Alternatively you can stick with the 6-dimensional phase space and have  $N$  points in it. In this latter picture you might cut up the phase space into cells and count how many particles are in each cell.

From this picture of phase space cell occupation numbers it is a small step to the thermodynamic probability. If the total number of particles is  $N$  and the number of particles in each cell is  $N_j$ , then the thermodynamic probability is given by,

$$\Omega = \frac{N!}{\prod_j N_j!} \approx \exp \left( N \ln N - \sum_j N_j \ln N_j \right)$$

The quantity,  $\Omega$ , is known as the *thermodynamic probability* or *thermodynamic weight* of the state of an ensemble (Note:  $\Omega$  is sometimes written as  $W$ ). The states with the largest values of  $\Omega$  are those that are most likely to occur.

However the states with the largest value of  $\Omega$  are also those with the most disorder – simply because there are so many configurations of the *microstates* to give one *macrostate*. This means that there must be relationship between the thermodynamic weight of a system and the entropy of a system.

Therefore if

$\Omega$  tends to a maximum,

then,

$S$  tends to a maximum.

### The Boltzmann-Planck entropy formula

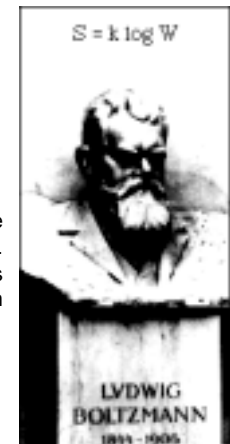
The Boltzmann-Planck equation for entropy is written,

$$S = k_B \ln \Omega$$

where  $\Omega$  is the *thermodynamic probability*, or the number of arrangements, of the state of the system. The states with the largest value of  $\Omega$  will be the ones most likely to occur. This equation is carved on Boltzmann's tombstone in Vienna.

### Entropy related to probability

To derive this we first consider an ensemble of a large number,  $v$ , of replica systems. Each of these individual systems can exist in one of,  $r$ , microstates, and for each microstate there is an associated probability,  $p_r$ , of the system being in that microstate.



Therefore, within the ensemble, the number of systems in the microstate,  $r$ , is simply,

$$\nu_r = \nu p_r$$

The thermodynamic probability of the ensemble is then given by,

$$\Omega_\nu = \frac{\nu!}{\nu_1! \nu_2! \nu_3! \dots \nu_r! \dots}$$

Applying this to the Boltzmann-Planck equation gives us,

$$\begin{aligned} S_\nu &= k_B \ln \Omega_\nu \\ &= k_B \ln \left( \frac{\nu!}{\nu_1! \nu_2! \nu_3! \dots \nu_r! \dots} \right) \\ &= k_B \left[ \nu \ln \nu - \sum_r \nu_r \ln \nu_r \right] \end{aligned}$$

which has been simplified using Stirling's 2-term approximation. The entropy of the ensemble is thus related to the entropy of a single system.

$$\begin{aligned} S &= \frac{1}{\nu} S_\nu = k_B \left[ \nu \ln \nu - \sum_r \nu_r \ln \nu_r \right] \\ &= k_B \left[ \ln \nu - \nu \sum_r p_r \ln p_r \right] \\ &\approx -k_B \sum_r p_r \ln p_r \quad (\text{for large } \nu) \end{aligned}$$

### The Schottky defect

At absolute zero the atoms in a crystalline solid are perfectly ordered. They inhabit regular lattice positions within the crystal.

As the temperature increases the atoms gain energy and are able to thermally vibrate. What are known as defects can occur within the crystal, where an atom has moved away from its original ordered position. These are known as *point defects*.

One particular type of point defect is the *Schottky defect*. In this case a displaced atom will migrate to the surface of the crystal, leaving a vacancy behind it.

Suppose we have a crystal composed of  $N$  atoms. Inside this crystal there are  $n$  defects. Each defect has an associated energy  $\varepsilon$ , since it takes energy to move the atom from the interior to the surface.

The energy associated with all the defects is,

$$E = n\varepsilon$$

What is the thermodynamic probability (or statistical weight) of this system ?

$$\Omega(n) = \frac{N!}{n!(N-n)!}$$

The entropy resulting from the Schottky defects will then be,

$$S(n) = k_B \ln \Omega(n) = k_B \ln \left( \frac{N!}{n!(N-n)!} \right)$$

The temperature of the crystal can be expressed in terms of the changes in entropy and energy of the crystal,

$$\begin{aligned} \frac{1}{T} &= \frac{\partial S}{\partial Q} = \frac{\partial S}{\partial E} \\ &= \frac{dS(n)}{dn} \frac{dn}{dE} \\ &= \frac{1}{\varepsilon} \frac{dS(n)}{dn} \end{aligned}$$

Using Stirling's two-term approximation we can write,

$$\begin{aligned} S(n) &= k_B [N \ln N - n \ln n - (N-n) \ln (N-n)] \\ \Rightarrow \frac{dS(n)}{dn} &= k [-\ln n + \ln (N-n)] \end{aligned}$$

So the temperature then becomes,

$$\frac{1}{T} = \frac{k_B}{\varepsilon} \ln \frac{N-n}{n}$$

Rearranging this gives us,

$$\frac{n}{N} = \frac{1}{e^{\epsilon/k_B T} + 1}$$

$$\therefore n = N e^{-\epsilon/k_B T}$$

This means that instead of expressing the temperature as a function of the number of Schottky defects we can now work out how many defects we can expect to find at a given temperature.

The defect energy is usually of the order of  $\epsilon \sim 1\text{eV}$ .

Temperature (K)	$n/N$
0 (absolute zero)	0
290 (room temperature)	$10^{-17}$
1000	$10^{-6}$

### Spin half systems and paramagnetism in solids

Suppose we have a system of  $N$  molecules in the form of a crystalline solid. If one of the atoms of the molecule has an unpaired electron then we can consider the effect of an external magnetic field applied to the solid.

An electron has an angular momentum  $\mathbf{s} = 1/2$ . In an applied magnetic field the electron spin will align with the magnetic field either parallel or anti-parallel to the field.

We therefore have a system of  $N$  spins, each of which can exist in either a *spin-up* or *spin-down* state.

The energies associated with the spin-up and spin-down states respectively are,

$$U \uparrow = -\mu_B B N \uparrow$$

$$U \downarrow = \mu_B B N \downarrow$$

so the total energy of the system is,

$$U = -\mu_B B N \uparrow + \mu_B B N \downarrow$$

$$= -(N \uparrow - N \downarrow) \mu_B B$$

There will be  $N \uparrow$  spins in the *spin-up* state and  $N \downarrow$  in the *spin-down* state. So for this two state system the *thermodynamic weight* will be,

$$\Omega = \frac{N!}{(N \uparrow)!(N \downarrow)!}$$

But we can write the spin-up and spin-down states in terms of the difference between them i.e.,

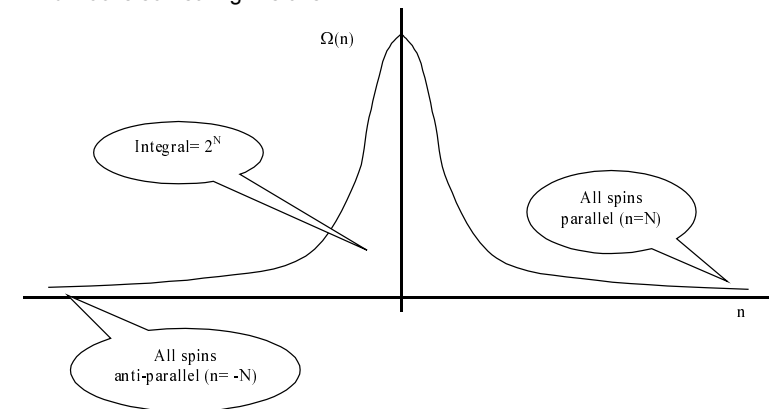
$$n = N \uparrow - N \downarrow$$

$$N = N \uparrow + N \downarrow$$

Therefore, the *thermodynamic weight*,  $\Omega$ , is,

$$\Omega(n) = \frac{N!}{\left(\frac{N+n}{2}\right)! \left(\frac{N-n}{2}\right)!}$$

which looks something like this.



The state equation for the internal energy of a system gives us,

$$dU = TdS - PdV$$

but when we are dealing with a solid the volume change,  $dV$ , is negligible and the number of particles,  $N$ , is constant.

$$dU = TdS$$

$$\Rightarrow T = \frac{dU}{dS}$$

$$\Rightarrow \frac{1}{T} = \frac{dS}{dU}$$

Using the Boltzmann-Planck entropy equation,  $S = k_B \ln \Omega$  we can write,

$$\begin{aligned} \frac{1}{T} &= \frac{dS}{dU} = k_B \frac{d(\ln \Omega(n))}{dU} \\ &= k_B \frac{d(\ln \Omega(n))}{dn} \frac{dn}{dU} \\ &= \frac{k_B}{2} \ln \left( \frac{N-n}{N+n} \right) \frac{dn}{dU} \end{aligned}$$

We know that,

$$\frac{dn}{dU} = -\frac{1}{\mu_B B}$$

therefore,

$$\frac{1}{T} = \frac{-k_B}{2} \ln \left( \frac{N-n}{N+n} \right) \frac{1}{\mu_B B}$$

Rearranging this we get,

$$\frac{-\mu_B B}{k_B T} = \frac{1}{2} \ln \left( \frac{N-n}{N+n} \right)$$

which can be written,

$$\left( \frac{N-n}{N+n} \right) = e^{-2x}$$

where,

$$x = \frac{\mu_B B}{k_B T}$$

Using the hyperbolic identity,

$$\tanh(x) = \left( \frac{e^x - e^{-x}}{e^x + e^{-x}} \right) = \frac{n}{N}$$

we finally have an expression for the total magnetisation of the solid.

$$M = n\mu_B = N\mu_B \tanh \left( \frac{\mu_B B}{k_B T} \right)$$

### Systems in thermal equilibrium and the canonical ensemble : the Boltzmann distribution

#### The Boltzmann distribution

Consider the thermal equilibrium between a system (1) and a large thermal reservoir (2) (heat bath).

At a particular point in time the system (1) will be in a certain microstate,  $r$ , with an associated energy,  $E_r$ . The total energy of the system is  $E_0$  so the energy of the thermal reservoir (2) is,

$$E_2 = E_0 - E_r$$

The probability of finding the system (1) in the microstate,  $r$ , is related to the thermodynamic weight.

$$P(r) = \frac{\Omega_2(E_0 - E_r)}{\sum_r \Omega_2(E_0 - E_r)}$$

Using the Taylor expansion of  $\ln(\Omega_2(E_0 - E_r))$  we get,

$$\ln(\Omega_2(E_0 - E_r)) = \ln \Omega_2(E_0) - \frac{\partial}{\partial E} [\ln(\Omega_2(E_0 - E_r))] E_r + \dots$$

However we have the definition that,

$$\frac{1}{k_B T} = \frac{\partial}{\partial E} [\ln(\Omega_2(E_0))] E_r$$

So we can write,

$$\Omega(E_0 - E_r) = \Omega(E_0) e^{-\frac{E_r}{k_B T}}$$

Substituting this into the equation for the probability of finding system (1) in a microstate,  $r$ , gives,

$$P(r) = \frac{\Omega(E_0) e^{-\frac{E_r}{k_B T}}}{\sum_r \Omega(E_0) e^{-\frac{E_r}{k_B T}}}$$

which gives the Boltzmann distribution,

$$P(r) = \frac{e^{-\frac{E_r}{k_B T}}}{\sum_r e^{-\frac{E_r}{k_B T}}}$$

### Single particle partition function, $Z$ , and $Z_N$ for localised particles : relation to Helmholtz function and other thermodynamic parameters

#### The single particle partition function, $Z$

The partition function,  $Z$ , is a weighted count of the number of possible microstates,  $n$ , that a particle can achieve, that takes account of the difficulty of reaching them.

$$Z = \sum_n e^{-\frac{E_n}{k_B T}}$$

#### The partition function for localised particles

When we are dealing with a large number of particles the partition function has to take into account all the possible combinations of the microstates for each particle.

However, the value of the partition function is dependent upon whether or not we can distinguish the particles we are dealing with.

1. Distinguishable particles : paramagnetic ions in a solid, distinguishable by their lattice positions.
2. Indistinguishable particles : gas particles.

#### The $N$ -particle partition function for distinguishable particles

Suppose we have three localised particles ( $a, b, c$ ) with a distinct set of possible energy levels for each particle ( $E_a, E_b, E_c$ ). The partition function for these three particles is given by,

$$Z_3 = \sum_{\text{all possibilities}} e^{-\frac{(E_a + E_b + E_c)}{k_B T}} \\ = \sum e^{-\frac{E_a}{k_B T}} \sum e^{-\frac{E_b}{k_B T}} \sum e^{-\frac{E_c}{k_B T}}$$

The particles all have the same set of energy levels so this becomes,

$$Z_3 = \left[ \sum e^{-\frac{E_a}{k_B T}} \right]^3 = Z_1^3$$

So for  $N$  distinguishable particles we have,

$$Z_N = (Z_1)^N$$

#### The $N$ -particle partition function for indistinguishable particles

If the particles are indistinguishable then there is no meaning to assigning separate energies to them since we cannot identify them.

The choice of energies  $E_a, E_b, E_c$  is then represented by one term in the sum over microstates, so the partition function for  $N$  indistinguishable particles is smaller by a factor  $N!$  than for  $N$  distinguishable particles.

*Distinguishable particles,*

$$Z_3 = \sum_{3 \text{ different energies}} e^{-\frac{(E_a + E_b + E_c)}{k_B T}} \\ + \sum_{2 \text{ different energies}} e^{-\frac{(E_a + E_b + E_c)}{k_B T}} \\ + \sum_{1 \text{ different energies}} e^{-\frac{(E_a + E_b + E_c)}{k_B T}}$$

*Indistinguishable particles,*

$$\begin{aligned}
 Z_3 &= \frac{1!}{3!} \sum_{3 \text{ different energies}} e^{-\frac{(E_a + E_b + E_c)}{k_B T}} \\
 &+ \frac{2!}{3!} \sum_{2 \text{ different energies}} e^{-\frac{(E_a + E_b + E_c)}{k_B T}} \\
 &+ \frac{3!}{3!} \sum_{1 \text{ different energies}} e^{-\frac{(E_a + E_b + E_c)}{k_B T}}
 \end{aligned}$$

Therefore for large  $N$ , where we can assume that no two particles share the same microstate, we have,

$$Z_N(\text{indistinguishable}) = \frac{Z_N(\text{distinguishable})}{N!}$$

So for indistinguishable particles, the  $N$ -particle partition function is given by,

$$Z_N = \frac{(Z_1)^N}{N!}$$

This is valid in the semi-classical approximation.

### Helmholtz function

We already have an expression for the Helmholtz function,

$$F = U - TS$$

and an expression for the entropy of a system in terms of the probability  $P_r$ ,

$$S = -k_B \sum_r P_r \ln P_r$$

where,

$$P_r = \frac{e^{-\frac{E_r}{k_B T}}}{Z}$$

so the entropy can be written,

$$\begin{aligned}
 S &= -k_B \sum_r \left( \frac{e^{-\frac{E_r}{k_B T}}}{Z} \right) \ln \left( \frac{e^{-\frac{E_r}{k_B T}}}{Z} \right) \\
 &= \frac{k_B}{Z} \sum_r \frac{E_r}{k_B T} e^{-\frac{E_r}{k_B T}} + k_B \sum_r \frac{e^{-\frac{E_r}{k_B T}}}{Z} \ln Z
 \end{aligned}$$

Simplifying this gives us,

$$S = \frac{\langle E \rangle}{T} + k_B \ln Z$$

so,

$$\begin{aligned}
 -k_B T \ln Z &= \langle E \rangle - TS \\
 &= U - TS \\
 \Rightarrow F &= -k_B T \ln Z
 \end{aligned}$$

The Helmholtz free energy,  $F$ , is a minimum for a system in thermodynamic equilibrium at constant  $T, V, N$ .

### Adiabatic cooling

The most common form of cooling is by refrigeration using process based on the Linde Liquifier. Heat is exchanged by compressing and expanding a working fluid.

At temperatures very close to absolute zero this operation becomes impossible since almost all systems will exist in a solid state.

Adiabatic demagnetisation is an important technique for reaching extremely low temperatures. The disorder and hence entropy of a paramagnetic salt is temperature dependent and magnetic field dependent.

- $S_{\text{Thermal}}$  is proportional to temperature
- $S_{\text{Magnetic}}$  is inversely proportional to magnetic field.

$$S_{\text{Total}} = S_{\text{Magnetic}} + S_{\text{Thermal}}$$

So if we reduce the magnetic field adiabatically, and so  $S_{\text{Magnetic}}$  increases, the total entropy must remain constant and the thermal entropy must decrease with a corresponding temperature drop.

The sample is enclosed in a liquid Helium heat bath from which it can be in contact or thermally isolated and placed within the pole pieces of an electromagnet. The magnetic field can be rapidly switched between a high value ( $B_1$ ) and a low value ( $B_0$ ).

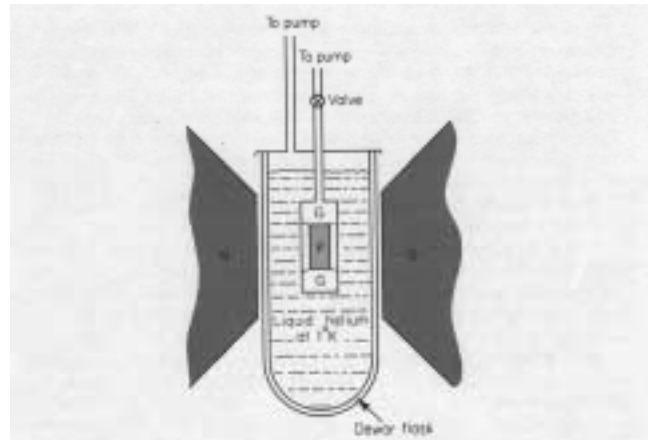


Fig. 5.19. Schematic diagram of apparatus for cooling by adiabatic demagnetization. P is the paramagnetic salt. The space G contains He gas or is evacuated. N and S are the poles of the magnet.

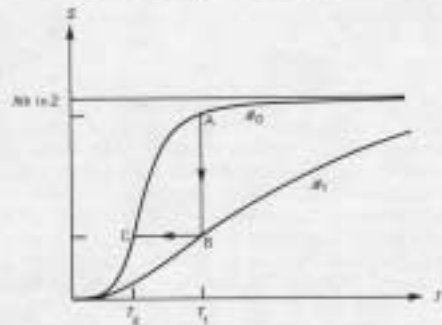


Fig. 5.20. The entropy-temperature curves for a paramagnetic salt, for different applied magnetic fields.

For a system in thermal equilibrium the Helmholtz function is a minimum,

$$F = U - TS$$

We can express the entropy of the system in terms of the partition function,

$$S = \frac{U - F}{T} \\ = \frac{U}{T} + k_B N \ln Z_1$$

The single particle partition function is easy to calculate since each particle can only be in one of two microstates, 'spin-up' or 'spin-down'.

$$Z_1 = e^{-\frac{\mu B}{k_B T}} + e^{\frac{\mu B}{k_B T}}$$

Simplifying this by making the substitution,

$$x = \frac{\mu B}{k_B T} \\ Z_1 = e^{-x} + e^x = 2 \cosh x$$

The internal energy of the system can also be expressed in similar terms.

$$U = \langle \mu \rangle NB \\ = (p_+ [-\mu] + p_- [+ \mu]) NB \\ = - \left( \frac{e^x}{Z_1} - \frac{e^{-x}}{Z_1} \right) \mu NB \\ = - \left( \frac{e^x - e^{-x}}{e^x + e^{-x}} \right) \mu NB \\ = - \mu NB \tanh x$$

So the entropy of the system is given by,

$$S = Nk_B [\ln(2 \cosh x) - x \tanh x]$$

So we see the entropy of the system is essentially a function of  $x$ , so for the adiabatic change,

$$\frac{B_1}{T_1} = \frac{B_0}{T_2}$$

Therefore if we reduce the magnetic field adiabatically (no change in entropy because no heat flow) the temperature of the system must reduce. This

enables us to reduce the temperature of the paramagnetic solid below that of the surrounding Helium bath.

### Thermodynamic parameters in terms of $Z$

The Helmholtz function tells us,

$$F = U - TS$$

and from this we can derive the state equation,

$$dF = -PdV - SdT - MdB$$

$$\therefore P = -\left(\frac{\partial F}{\partial V}\right)_{T,B}$$

$$\therefore S = -\left(\frac{\partial F}{\partial T}\right)_{V,B}$$

$$\therefore M = -\left(\frac{\partial F}{\partial B}\right)_{T,V}$$