

# Section 5

## Further Thermodynamics

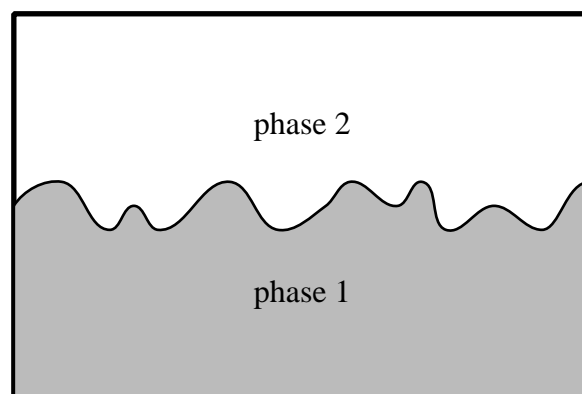
### 5.1 Phase equilibrium

#### 5.1.1 Conditions for equilibrium coexistence

It is an observed fact that the physical state of a system can sometimes be changed dramatically when its external conditions are changed only slightly. Thus ice melts when the temperature is increased from slightly below  $0^{\circ}\text{C}$  to slightly above this temperature. Different physical states of the same substance are referred to as *phases* and the study of transitions between phases is one of the most interesting problems in statistical thermodynamics. This is partly because the question of predicting when and how a phase transition will occur is still not a fully solved problem. There is the further point that a comprehensive understanding of phase transition phenomena might have wider application to such things as the outbreak of a war or a stock market crash.

Very generally, phase transitions are due to interactions between the constituent particles of a system. The model-dependence of the behavior would suggest that full understanding can only come from a statistical mechanical study, not from thermodynamics. However there are many aspects of phase transitions which seem to be general and common to many systems. Macroscopic thermodynamics is of help here since it *is* model-independent and it connects seemingly unrelated properties of the system. This frees us to concentrate on the few thermodynamic variables of the system instead of getting bogged down in the microscopic detail.

We start by considering the conditions for equilibrium to exist between two phases of the same substance — such as ice and water, for example.



*two phases in coexistence*

The fact that the two phases are in intimate contact with one another means that they must be at the same temperature and pressure. And we know that the condition for equilibrium in a system at given temperature and pressure is that the Gibbs free energy be a minimum. Note that this condition is independent of the nature of the constraints on the composite system. To summarise

- Phase equilibrium is determined by minimising the Gibbs free energy  $G$ . This is regardless of the constraints on the system.

We shall now make an important connection with the chemical potential. From the definition of  $G$  we know that its differential expression is

$$dG = -SdT + Vdp + \mu dN$$

and that the proper variables for  $G$  are then  $T$ ,  $p$  and  $N$ . But  $G(T, p, N)$  is an extensive quantity. This means that

$$G(T, p, N) = NG(T, p, 1)$$

since both the other variables  $T$  and  $p$  are intensive. From the expression for  $dG$  we see that  $\mu$  may be specified as

$$\mu = \left. \frac{\partial G}{\partial N} \right|_{T,p}$$

so that

$$\begin{aligned} \mu &= \left. \frac{\partial}{\partial N} \right|_{T,p} G(T, p, N) \\ &= \left. \frac{\partial}{\partial N} \right|_{T,p} NG(T, p, 1) \\ &= G(T, p, 1). \end{aligned}$$

In other words the chemical potential is none other than the Gibbs free energy per particle, which we shall sometimes denote by  $g$ .

The equilibrium state of the system is that for which  $G$  is a minimum:

$$dG = d(G_1 + G_2) = 0$$

Now if there are  $N_1$  particles in phase 1 and  $N_2$  particles in phase 2 then since

$$G_1 = \mu_1 N_1 \quad \text{and} \quad G_2 = \mu_2 N_2,$$

the equilibrium condition may be written as

$$d(\mu_1 N_1 + \mu_2 N_2) = 0.$$

The total number of particles in the composite system is fixed:

$$N_1 + N_2 = \text{const.}$$

So if we consider movement of particles between the phases, then

$$\left. \begin{aligned} \mu_1 dN_1 + \mu_2 dN_2 &= 0 \\ dN_1 + dN_2 &= 0 \end{aligned} \right\}$$

or

$$(\mu_1 - \mu_2) dN_1 = 0,$$

which can only be satisfied if

$$\mu_1 = \mu_2.$$

In other words, when equilibrium is established between two phases, not only are the temperature and the pressure equalised, but the chemical potentials are the same as well.

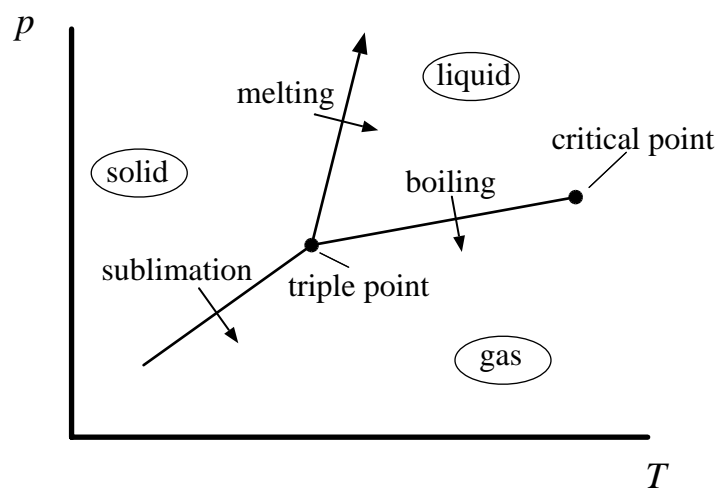
In retrospect this is obvious since  $\mu$  is the “force” which drives particle flow.

- $\mu_1 < \mu_2$  means particles flow from phase 2 to phase 1
- $\mu_1 > \mu_2$  means particles flow from phase 1 to phase 2.

So when equilibrium is established then there is no net flow of particles between the phases.

### 5.1.2 The phase diagram

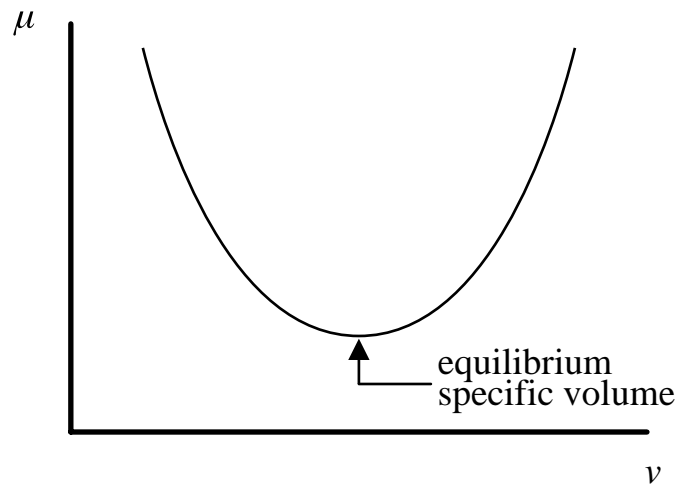
The phase diagram of a typical  $p - V - T$  system is shown in the figure below. There are three distinct phases: solid, liquid and gas. The lines separating the phases are the transition lines: the melting line, the boiling line and the sublimation line. When a transition line is crossed there is a change of phase. Along a transition line one has a coexistence of the two phases. And at a single point one can have a coexistence of three phases. This is called the triple point.



typical phase diagram

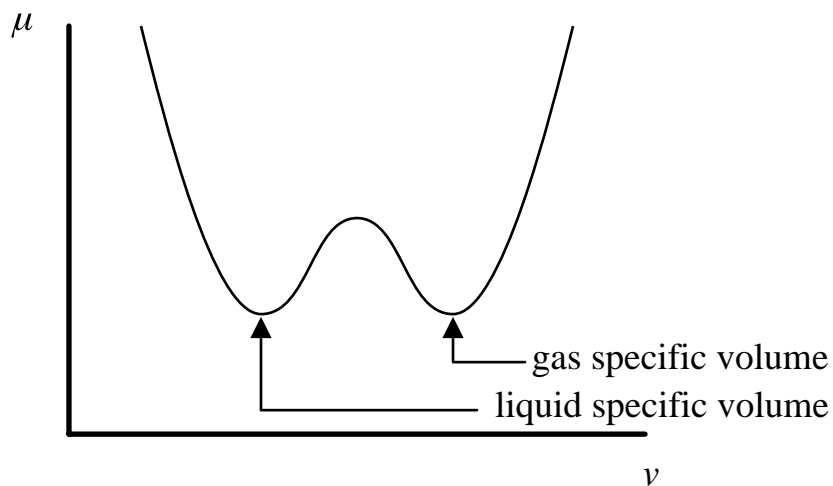
The symmetry of the liquid and the gas phases are the same. For this reason the transition line between liquid and gas, the boiling line, can terminate. The termination point is called the *critical point*. Conversely the symmetry of the solid and the liquid/gas phases are different. Now symmetry cannot change continuously. This means that the melting line cannot terminate; it goes on forever.

The equilibrium density of a system at specified temperature and pressure is found by minimising the Gibbs free energy of the system. In other words the Gibbs free energy (or the Gibbs free energy per particle  $\mu$ ) will be a minimum as a function of density (or the specific volume  $\nu$ ).



*equilibrium density of a system*

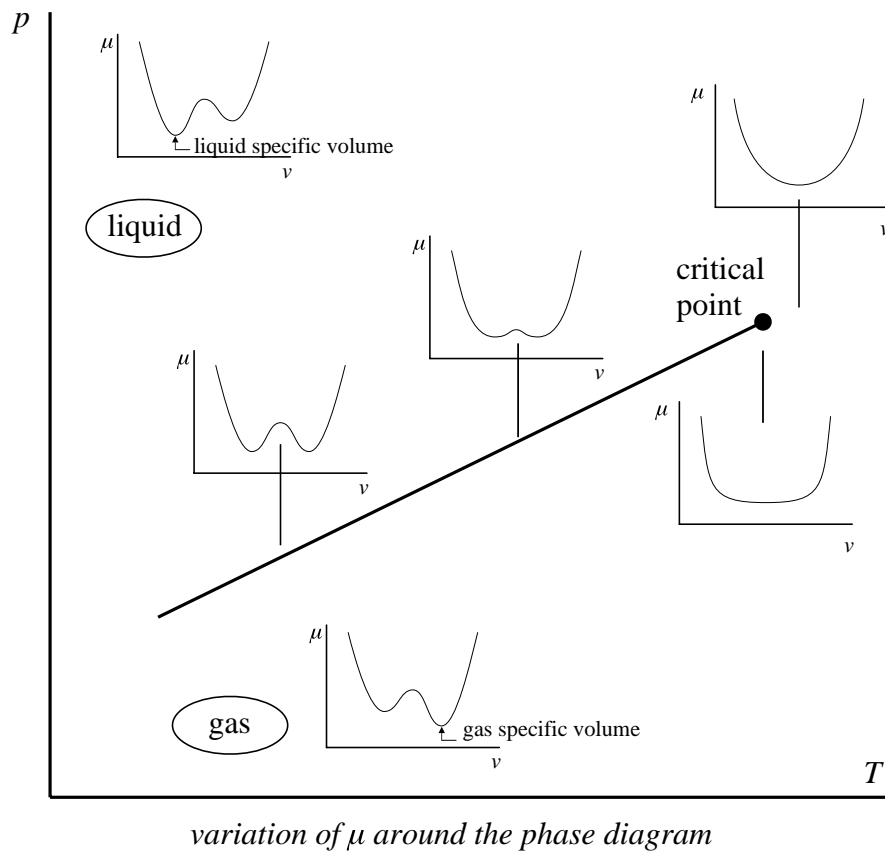
Now on a transition line two phases, with different densities, can coexist. In terms of the Gibbs free energy this is telling us that there must be *two* minima of equal depth, at two different densities. So there is a double minimum.



*coexistence of two phases*

We can extend these arguments to other regions of the phase diagram.

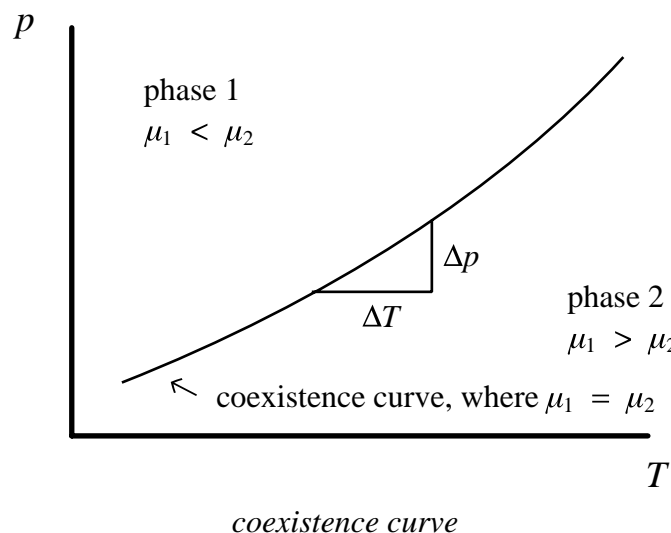
- Along the coexistence curve there will be two minima of equal depth.
- Moving along the coexistence curve towards the critical point, the two minima become closer together as the liquid and gas densities become closer.
- At the critical point the two minima coalesce; they become degenerate.
- Away from the coexistence curve the two minima will be of unequal depth. In the liquid phase the higher-density minimum will be lower, while in the gas phase the lower-density minimum will be lower.



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### 5.1.3 Clausius-Clapeyron equation

Equilibrium will be maintained between two phases over a range of temperatures so long as particles can flow so as to equalise the chemical potentials. This gives a line of equilibrium coexistence in the  $T - p$  plane, as we have seen.



We shall examine the differential relation satisfied by the coexistence curve. This is a relation which holds between the phases as the external conditions are varied.

Along the coexistence curve we must have  $\mu_1 = \mu_2$  although the value of  $\mu_1$  and  $\mu_2$  will be different as one moves along the curve.

For a small displacement along the coexistence curve we must have

$$\Delta\mu_1 = \Delta\mu_2$$

or, in terms of  $\Delta T$  and  $\Delta p$ :

$$\left. \frac{\partial\mu_1}{\partial T} \right|_p \Delta T + \left. \frac{\partial\mu_1}{\partial p} \right|_T \Delta p = \left. \frac{\partial\mu_2}{\partial T} \right|_p \Delta T + \left. \frac{\partial\mu_2}{\partial p} \right|_T \Delta p.$$

Now since  $\mu$  is the Gibbs free energy per particle, we can write

$$\mu = e - Ts + pv$$

where  $e$  is the energy per particle  
 $s$  is the entropy per particle  
 $v$  is the volume per particle.

The derivatives of  $\mu$  are then given by

$$\left. \frac{\partial\mu}{\partial T} \right|_p = -s \quad \left. \frac{\partial\mu}{\partial p} \right|_T = v$$

so that we have

$$-s_1\Delta T + v_1\Delta p = -s_2\Delta T + v_2\Delta p$$

or

$$(s_2 - s_1)\Delta T = (v_2 - v_1)\Delta p.$$

Letting  $\Delta T$  and  $\Delta p$  tend to zero, we obtain the slope of the coexistence curve as

$$\frac{dp}{dT} = \frac{s_2 - s_1}{v_2 - v_1}$$

or

$$\frac{dp}{dT} = \frac{\Delta s}{\Delta v}$$

where  $\Delta s$  is the change in specific entropy and  $\Delta v$  is the change in specific volume either side of the coexistence line.

The entropy change per particle is the difference in a particle's entropy in the two phases at a specified temperature and pressure. We are thus considering an entropy change, or heat flow at constant temperature. This is related to the *latent heat* of transformation:

$$l_{1 \rightarrow 2} = T(s_2 - s_1)$$

where  $l$  is the latent heat per particle.

We can then write the Clausius-Clapeyron equation as

$$\frac{dp}{dT} = \frac{l}{T\Delta v}.$$

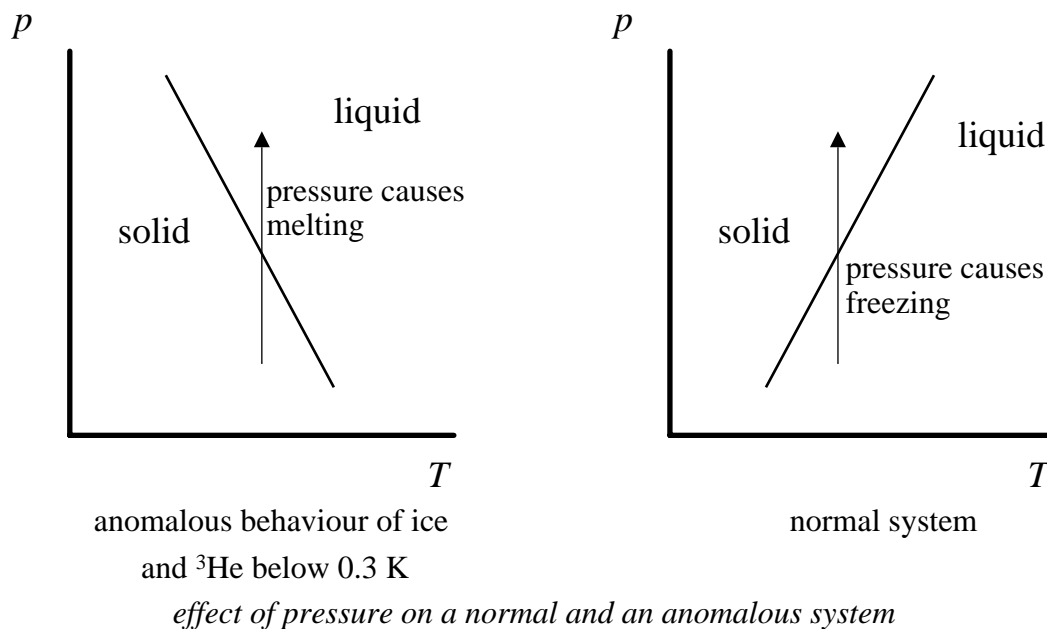
In melting one usually finds:

- The entropy increases — the liquid is more disordered than the solid —  $\Delta s$  is positive.
- On melting a solid expands —  $\Delta v$  is positive.

So the slope  $dp/dT$  of the coexistence curve is usually positive. There are two notable exceptions from this normal behaviour.

In  $^3\text{He}$  below about 0.3 K the solid is more disordered than the liquid! Thus  $\Delta s$  is negative. But solid  $^3\text{He}$  does expand on melting, so  $\Delta v$  is positive. So the slope  $dp/dT$  of the coexistence curve is negative.

When ice melts the liquid is indeed more disordered than the solid;  $\Delta s$  is positive. But ice *contracts* on melting;  $\Delta v$  is negative. So here also slope  $dp/dT$  of the coexistence curve is negative. This explains why ice can be melted by increasing the pressure — a fact of importance to ice skaters but rather unfortunate for motorists.



#### 5.1.4 Saturated vapour pressure

From the Clausius-Clapeyron equation we may obtain an approximate expression for the vapour pressure over a solid or a liquid. Along the coexistence curve there are no free variables. Thus so long as both phases are present,  $p$  is a *unique* function of  $T$ . In fact at low temperatures (from about 5 K to about 0.3 K) the standard experimental temperature scale is defined in terms of the vapour pressure above liquid helium. Tables and a formula are given for this. (For temperatures below 0.3 K the pressure along the solid-liquid coexistence of  $^3\text{He}$  is used for thermometry.)

We shall use the Clausius-Clapeyron relation to derive an approximate expression relating temperature and pressure of a saturated vapour. So we start from

$$\frac{dp}{dT} = \frac{l}{T\Delta v}$$

and we make the following assumptions:

- The specific volume of the condensed phase can be neglected in comparison to that of the vapour.

$$\Delta v = v_2 - v_1 \approx v_2.$$

- The vapour may be treated as an ideal gas.

$$pv_2 = kT. \quad (v_2 \text{ is the volume per particle})$$

- The latent heat is independent of temperature.

$$l = \text{const.}$$

Using these approximations in the Clausius-Clapeyron equation gives

$$\frac{dp}{dT} = \frac{lp}{kT^2}.$$

Writing this as

$$\frac{1}{p} \frac{dp}{dT} = \frac{l}{kT^2}$$

we can integrate to obtain

$$\ln p = -\frac{l}{kT} + \text{const}$$

or

$$p = p_0 \exp \frac{-l}{kT}.$$

Thus the vapour pressure is a rapidly increasing function of temperature. This also gives a rather convenient way of measuring the latent heat of vapourisation, which is a measure of the binding energy in the condensed phase.

There are transitions for which  $\Delta S$  and  $\Delta V$  are zero. Clearly there is no latent heat associated with such transitions. These are called *second order* transitions, while those considered above are called *first order* transitions. Second order transitions are studied in PH361.

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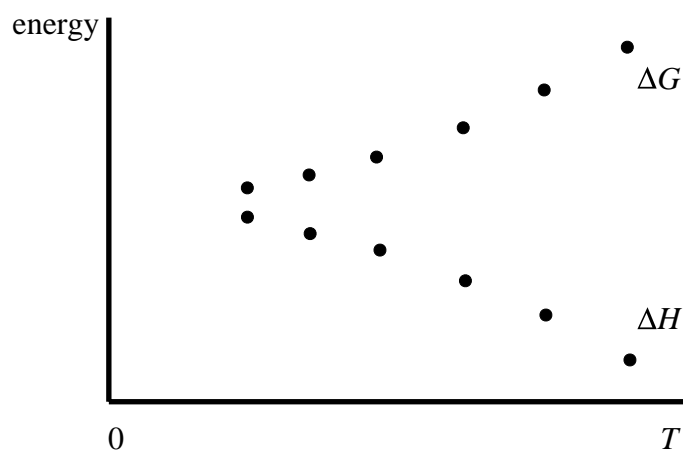
## 5.2 The Third Law of thermodynamics

### 5.2.1 History

The third law of thermodynamics arose as the result of experimental work in chemistry, principally by the famous chemist Nernst. He published what he called his “heat theorem” in 1906.

Nernst measured the change in Gibbs free energy and the change in enthalpy for chemical reactions which started and finished at the same temperature. At lower and lower temperatures he found that the changes in  $G$  and the changes in  $H$  became closer and closer.





Nernst's observations

Nernst was led to conclude that at  $T = 0$  the changes in  $G$  and  $H$  were the same. And from some elementary thermodynamic arguments he was able to infer the behaviour of the entropy at low temperatures.

Changes in  $H$  and  $G$  are given by

$$\Delta H = T\Delta S + V\Delta p$$

$$\Delta G = -S\Delta T + V\Delta p.$$

Thus  $\Delta G$  and  $\Delta H$  are related by

$$\Delta G = \Delta H - T\Delta S - S\Delta T$$

and if the temperature is the same before and after,  $\Delta T = 0$ , so then

$$\Delta G = \Delta H - T\Delta S.$$

This is a very important equation for chemists.

Now Nernst's observation may be stated as

$$\Delta H - \Delta G \rightarrow 0 \quad \text{as} \quad T \rightarrow 0,$$

which he realised implied that

$$T\Delta S \rightarrow 0 \quad \text{as} \quad T \rightarrow 0.$$

### 5.2.2 Entropy

On the face of it this result is no surprise since the factor  $T$  will ensure the product  $TdS$  goes to zero. But Nernst took the result further. He studied *how fast*  $\Delta H - \Delta G$  tended to zero. And his observation was that it went faster than linearly. In other words he concluded that

$$\frac{\Delta H - \Delta G}{T} \rightarrow 0 \quad \text{as} \quad T \rightarrow 0.$$

So even though  $1/T$  was getting bigger and bigger, the quotient  $(\Delta H - \Delta G)/T$  still tended to zero.

But we know that

$$\frac{\Delta H - \Delta G}{T} = \Delta S.$$

So from this Nernst drew the conclusion

$$\Delta S \rightarrow 0 \quad \text{as} \quad T \rightarrow 0.$$

The entropy change in a process tends to zero at  $T = 0$ . The entropy thus remains a constant in any process at absolute zero. We conclude:

- The entropy of a body at zero temperature is a constant, independent of all other external parameters.

This was the conclusion of Nernst, sometimes called Nernst's heat theorem. It was subsequently to be developed into the Third Law of thermodynamics.

### 5.2.3 Quantum viewpoint

From the purely macroscopic perspective the third Law is as stated above: at  $T = 0$  the entropy of a body is a constant. And many conclusions can be drawn from this. One might ask the question "what is the constant?". However we do know that thermodynamic conclusions about measurable quantities are not influenced by any such additive constants since one usually differentiates to find observables. (But a constant of minus infinity, as we found for the classical ideal gas, might be problematic.)

If we want to ask about the constant then we must look into the microscopic model for the system under investigation. Recall the Boltzmann expression for entropy:

$$S = k \ln \Omega$$

where  $\Omega$  is the number of microstates in the macrostate. Now consider the situation at  $T = 0$ . Then we know the system will be in its ground state, the lowest energy state. But this is a *unique* quantum state. Thus for the ground state

$$\Omega = 1$$

and so

$$S = 0.$$

Nernst's constant is thus zero and we then have the expression for the Third Law:

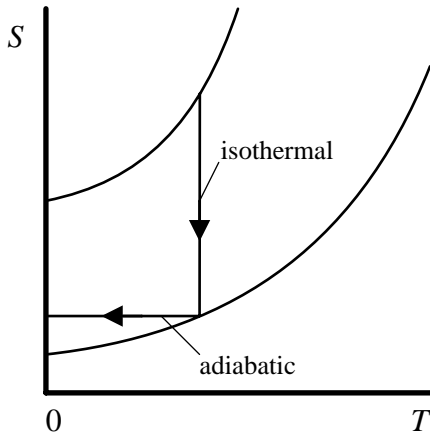
- As the absolute zero of temperature is approached the entropy of all bodies tends to zero.

We note that this applies specifically to bodies which are in *thermal equilibrium*. The Third Law can be summarised as

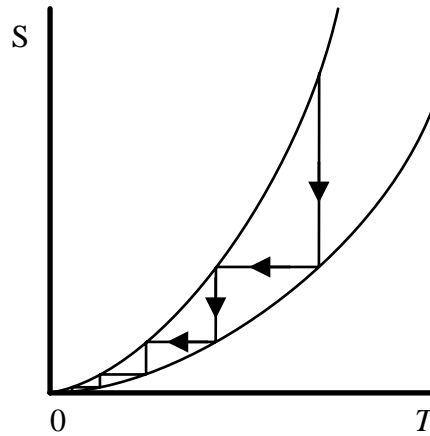
$$\frac{\partial S}{\partial \text{anything}} \rightarrow 0 \quad \text{as} \quad T \rightarrow 0.$$

### 5.2.4 Unattainability of absolute zero

The Third Law has important implications concerning the possibility of cooling a body to absolute zero. Let us consider a sequence of adiabatic and isothermal operations on two systems, one obeying the Third Law and one not.



System not obeying Third Law  
 One can get to  $T = 0$  in 2 steps

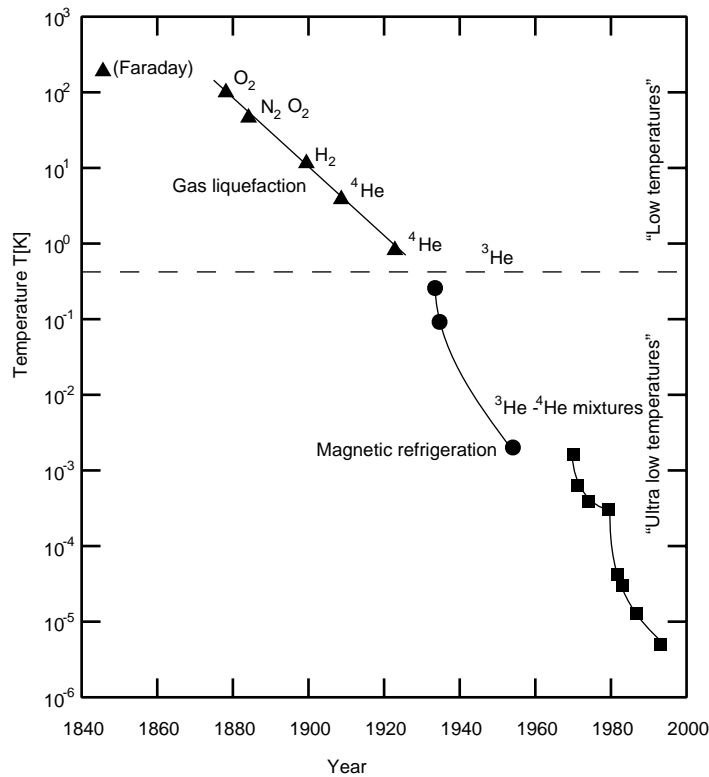


System obeying Third Law  
 One can not get to  $T = 0$  in a finite number of steps

*approaching absolute zero*

Taking a sequence of adiabatics and isothermals between two values of some external parameter we see that the existence of the Third Law implies that you cannot get to  $T = 0$  in a finite number of steps. This is, in fact, another possible statement of the Third Law.

Although one cannot get all the way to  $T = 0$ , it is possible to get closer and closer. The following graph indicates the success in this venture.



*the road to absolute zero*

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### 5.2.5 Heat capacity at low temperatures

The Third Law has important consequences for the thermal capacity of bodies at low temperatures. Since

$$C = \frac{\partial Q}{\partial T} \\ = T \frac{\partial S}{\partial T},$$

and the Third Law tells us that

$$\frac{\partial S}{\partial T} \rightarrow 0 \quad \text{as} \quad T \rightarrow 0,$$

we then have

$$C \rightarrow 0 \quad \text{as} \quad T \rightarrow 0.$$

Classical models often give a constant thermal capacity. Recall that for an ideal gas

$$C_V = \frac{3}{2}Nk$$

independent of temperature. The Third Law tells us that this cannot hold at low temperatures. And indeed we saw that for a Fermi gas (and a Bose gas?)  $C_V$  does indeed go to zero at  $T = 0$ .

### 5.2.6 Other consequences of the Third Law

Most “response functions” or susceptibilities – generalised spring constants – go to zero or a constant as  $T \rightarrow 0$  as a consequence of the Third Law. This is best seen by examining the relevant Maxwell relation. For example consider the thermal expansion coefficient. The Maxwell relation here is

$$\left. \frac{\partial V}{\partial T} \right|_p = - \left. \frac{\partial S}{\partial p} \right|_T.$$

The right hand side is zero by virtue of the Third Law. Thus we conclude that

$$\left. \frac{\partial V}{\partial T} \right|_p \rightarrow 0 \quad \text{as} \quad T \rightarrow 0;$$

the expansion coefficient goes to zero.

An interesting example is the susceptibility of a paramagnet. The connection with the model  $p - V$  system is made via

$$M \rightarrow p \\ B \rightarrow V.$$

The magnetic susceptibility is (neglecting factors of  $\mu_0$ )

$$\chi = \frac{\partial M}{\partial B} \\ \rightarrow \frac{\partial p}{\partial V}.$$

There is no Maxwell relation for this, but consider the variation of the susceptibility with temperature:

$$\frac{\partial \chi}{\partial T} = \frac{\partial^2 M}{\partial T \partial B}$$

$$\rightarrow \frac{\partial^2 p}{\partial T \partial V}.$$

The order of differentiation can be reversed here. In other words

$$\frac{\partial}{\partial B} \frac{\partial M}{\partial T} \rightarrow \frac{\partial}{\partial V} \frac{\partial p}{\partial T}.$$

And now we do have a Maxwell relation:

$$\left. \frac{\partial p}{\partial T} \right|_V = \left. \frac{\partial S}{\partial V} \right|_T \quad \leftarrow \quad \left. \frac{\partial M}{\partial T} \right|_V = \left. \frac{\partial S}{\partial B} \right|_T.$$

The Third Law tells us that the right hand side of these equations goes to zero as  $T \rightarrow 0$ . We conclude then that

$$\frac{\partial \chi}{\partial T} \rightarrow 0 \quad \text{as} \quad T \rightarrow 0$$

or

$$\chi \rightarrow \text{const} \quad \text{as} \quad T \rightarrow 0.$$

The Third Law tells us that the magnetic susceptibility becomes constant as  $T \rightarrow 0$ . But what did Curie's law give? This stated

$$\chi = \frac{C}{T}$$

so that

$$\chi \rightarrow \infty \quad \text{as} \quad T \rightarrow 0 !!$$

This is *completely incompatible* with the Third Law.

But Curie's law is a specifically high temperature result. Also it does not consider the interactions between magnetic moments which *have* to occur.

In fluid systems, where the particles must be treated as delocalised, the statistics will also have an effect. Recall the behaviour of fermions at low temperatures. We saw that very roughly only a fraction  $T/T_F$  of the particles were free and available to participate in "normal" behaviour. We then expect that the Curie law behaviour will be modified to

$$\chi \sim \left( \frac{T}{T_F} \right) \times \frac{C}{T}$$

or

$$\chi \sim \frac{C}{T_F}$$

which is indeed a constant, in conformity with the Third Law. This result is correct, but a numerical calculation must be done to determine the numerical constants involved.

### 5.2.7 Pessimist's statement of the laws of thermodynamics

As we have now covered all the laws of thermodynamics we can present statements of them in terms of what they prohibit in the operation of Nature.

- **First Law:** You cannot convert heat to work at greater than 100% efficiency
- **Second Law:** You cannot even achieve 100% efficiency — except at  $T = 0$ .
- **Third Law:** You cannot get to  $T = 0$ .

This is a simplification, but it encapsulates the underlying truths, and it is easy to remember.

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