# CHAPTER 16
## NERNST'S HEAT THEOREM AND THE THIRD LAW OF THERMODYNAMICS

16.1  *Nernst's Heat Theorem*

At the beginning of the twentieth century, Walther Nernst (Nobel Prize in Chemistry 1920) had investigated heat capacities and heats of reaction at progressively lower temperatures.  As a result of his studies, he enunciated an important principle that initially was restricted to the behaviour of reactions involving solids and liquids but which is now believed to apply to all processes and substances.

The subject of chemical thermodynamics is dealt with more fully in Chapter 17, but for the present we shall note that some chemical reactions require an input of heat to initiate them; other chemical reactions generate heat.  The former are known as *endothermic* reactions; the latter are *exothermic* reactions.  If the reaction takes place at constant pressure (i.e. on an open laboratory bench) the heat gained or lost is an increase or decrease in *enthalpy H*.  The *heat of reaction* is usually given as $\Delta H$, being positive for an endothermic reaction (in which the system gains heat) and negative for an exothermic reaction.  It should be noted that spontaneous reactions are by no means always exothermic; some spontaneous reactions result in the absorption of heat from their surroundings and in a corresponding increase of enthalpy.

Nernst had noticed that, at progressively lower temperatures, the change in enthalpy and the change in the Gibbs function during a chemical reaction become more and more equal.  And (as we shall see, what amounts to the same thing) the *rate of change of the Gibbs function with temperature* becomes less and less as the temperature is lowered. That this amounts to the same thing is evident from the Gibbs-Helmholtz relation

$$\Delta H \;=\; \Delta G \;-\; T\!\left(\frac{\partial(\Delta G)}{\partial T}\right)_{P}.$$
<div align="right">16.1.1</div>

What Nernst proposed was that, in the limit, as the temperature approaches zero, the changes in the enthalpy and Gibbs function are equal − or, what amounts to the same thing, the temperature rate of change of the Gibbs function at constant pressure approaches zero at zero temperature.  And since

$$\left(\frac{\partial(\Delta G)}{\partial T}\right)_{P} \;=\; -\Delta S,$$
<div align="right">16.1.2</div>

this implies that *chemical reactions at a temperature of absolute zero take place with no change of entropy.*  This is *Nernst's Heat Theorem.*

Planck later extended this to suppose that, not only does $\Delta G \rightarrow \Delta H$, but that, as $T \rightarrow 0$, the enthalpy and the Gibbs function of the system approach each other asymptotically in such a manner that, in the limit, as $T \rightarrow 0$, $G \rightarrow H$ and $(\partial G / \partial T)_P \rightarrow 0$.

This has a number of consequences. For example, until now, we had defined only what is meant by a *change in entropy*. In particular, in order to state what *the* entropy of a system is at some temperature, we would need to know what the entropy is at a temperature of zero kelvin. In Sections 12.8 and 12.9 we attempted to calculate the change in the Helmholtz and Gibbs functions as a system was changed from one state to another. We found that the right hand sides of equations 12.9.9 and 12.9.11 for calculating the changes in these functions contained the entropy. We later went on to show how we could calculate the difference in entropy in some state to that at zero temperature, but there was still a matter of an arbitrary constant, namely – what is the entropy at zero temperature? We now have the answer, resulting *from the observed behaviour of* $(\partial G / \partial T)_P$ $[=-S]$ as the temperature approaches zero – namely that the arbitrary constant is no longer arbitrary, and the entropy approaches zero as the temperature approaches zero.

Another consequence is

## 16.2 *The Third Law of Thermodynamics*

Nernst's heat theorem and Planck's extension of it, while originally derived from observing the behaviour of chemical reactions in solids and liquids, is now believed to apply quite generally to any processes, and, in view of that, it is time to reconsider our description of adiabatic demagnetization. We see immediately that figure XV.1 needs to be redrawn to reflect the fact that the entropy of the substance approaches zero whether or not it is situated in a magnetic field. The revised drawing is shown as figure XVI.1, in which I have drawn three consecutive magnetization-demagnetization operations, and it will be readily seen that we shall never reach a temperature of exactly zero in a finite number of operations.

The same applies to any operation in which we attempt to lower the temperature by a series of isothermal constraints that decrease the entropy followed by adiabatic relaxations – whether we are compressing a gas isothermally and then decompressing it adiabatically, or stretching a rubber band isothermally and loosening it adiabatically. In all cases, owing to the convergence of the two entropy curves at zero temperature, we are led to conclude:

*It is impossible to reduce the temperature of a material body to the absolute zero of temperature in a finite number of operations.*

This is the *Third Law of Thermodynamics*, and it is an inevitable consequence of Planck's extension of Nernst's Heat Theorem.
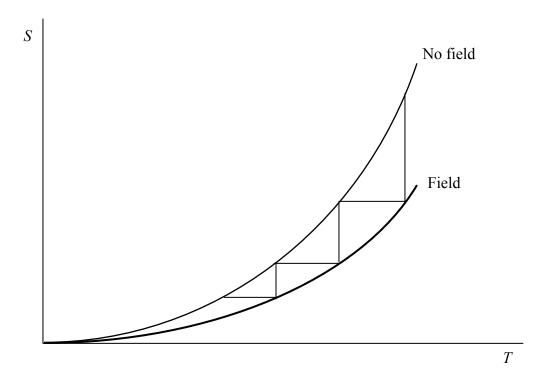
FIGURE XVI.1

This is usually taken to mean that it is impossible ever to reduce the temperature of anything to absolute zero. From a practical point of view, that may be true, though that is not strictly what the third law says. It says that it is impossible to do it in a *finite number* of operations. I cannot help but think of a bouncing ball (see Classical Mechanics Chapter V), in which the ball bounces an infinite number of times before finally coming to rest after a finite time. After every bounce, there are still an infinite number of bounces yet to come, yet it is all over in a finite time. Now, perhaps some reader of these notes one day will devise a method of performing an infinite number of isothermal stress/adiabatic relaxation operations in a finite time, and so attain absolute zero.

The third law also talks about a finite number of *operations* – by which I take it is meant operations such as an entropy-reducing constraint followed by an adiabatic relaxation. I am not sure to what extent this applies to processes such as *laser cooling*. In such experiments a laser beam is directed opposite to an atomic beam. The laser frequency is exactly equal to the frequency need to excite the atoms to their lowest excited level, and so it stops the atoms in their tracks. As the atoms slow down, the required frequency can be changed to allow for the Doppler effect. Such experiments have reduced the temperature to a fraction of a nanokelvin. These experiments do not seem to be of the sort of experiment we had in mind when developing the third law of thermodynamics. We might well ask ourselves if it is conceptually possible or impossible to reduce the speeds of a collection of atoms to zero for a finite period of time. We might argue that it *is*

conceptually possible – but then we may remember that atoms attract each other (van der Waals forces), so, if all the atoms are instantaneously at rest, they will not remain so. Of course if we had an ideal gas (such as a real gas extrapolated to zero pressure!) such that there are no forces between the molecules, the concept of zero temperature implies that all the atoms are stationary – i.e. each has a definite position and zero momentum. This is, according the Heisenberg's uncertainty principle, inconceivable. So I leave it open as a subject for lunchtime conversations exactly how strictly the third law prevents us from ever attaining the absolute zero of temperature.

*Exercise.* If the kinetic temperature of a set of hydrogen atoms is reduced to a tenth of a nanokelvin, what is the root-mean-square speed of the atoms?