CHAPTER 11

MAGNETIC SYSTEMS

§11.01 *Introduction*

In order to apply thermodynamics to magnetic systems we have merely to extend our previous formulae by including extra terms for the magnetic work. In principle the procedure is straightforward and should cause no difficulty. There is however a serious incidental difficulty, namely that of finding the correct general expression for magnetic work. We should expect to be able to discover such an expression by consulting any reputable text-book on electromagnetism. Unfortunately this is far from the case. The treatment given in most text-books is altogether inadequate. In most cases the derivations of formulae for magnetic work assume either explicitly or implicitly that the permeability of each piece of matter is a constant, whereas from a thermodynamic viewpoint one of the questions of greatest interest is how the permeability varies with the temperature. It is therefore desirable, if not essential, to start from formulae which are not restricted to the assumption that the permeability of each piece of matter is invariant. In many, if not most, text-books on electromagnetism the treatment of magnetic work suffers from other even more serious defects. In some text-books the treatment is based on a discussion of permanent magnets imagined to be constructed by bringing together (reversibly?!) from infinity an infinite number of infinitesimal magnetic elements. Actually a permanent magnet is an idealization far from reality. It is true that magnets can be made which are nearly permanent with respect to changes in position, but they are never permanent with respect to changes of temperature. Increase of temperature is usually accompanied by an irreversible loss of magnetization. Whatever may be the use of the conception of a permanent magnet in the theory of such instruments as compasses, galvanometers, and dynamos, it is not a useful conception as a basis for the analysis of magnetic work when changes of temperature may be important. The worst text-books give formulae for magnetic work which not only are of restricted applicability, but even contain wrong signs. Others confuse the external magnetic field $\boldsymbol{B}_e$ with the local internal field $\boldsymbol{B}$. Fortunately there are a few text-books* on electromagnetism which give a clear correct treatment of magnetic work. Here we shall assume the correct formula for magnetic work after first recalling the physical meaning of the several electromagnetic quantities involved and how they are related to one another.

§11.02 *Fundamental electromagnetic vectors*

As elsewhere in this book we use the rationalized system of electromagnetic quantities. We recall that the strength and direction of an electrostatic field is described at each point by a vector $\boldsymbol{E}$ such that the force acting on a small stationary test charge Q placed at this point is $Q\boldsymbol{E}$. This vector $\boldsymbol{E}$ is called the *electric field strength.* The analogous magnetic vector describing the force acting on a small test element of current is denoted by $\boldsymbol{B}$ and has the property† that the force on each element $\mathrm{d}\boldsymbol{s}$ of a linear conductor of current i is given by the vector product $i\mathrm{d}\boldsymbol{s}\times\boldsymbol{B}$. This vector $\boldsymbol{B}$ is called the *magnetic induction.*

§11.03 *Permittivity and permeability in a vacuum*

In a vacuum the value of $\boldsymbol{E}$ at each point is determined by the distribution of electric charges and is the sum of independent contributions from each charge. The contribution to $\boldsymbol{E}$ of a charge Q at a distance r is directed along r and is of magnitude

$$Q/4\pi\varepsilon_0 r^2 \tag{11.03.1}$$

where ε_0 is a universal constant called the *rationalized permittivity of a vacuum*. Alternatively we may say that each charge Q makes an additive contribution

$$Q/4\pi\varepsilon_0 r \tag{11.03.2}$$

to the *electrostatic potential* ψ and that $\boldsymbol{E}$ is then determined by

$$\boldsymbol{E} = -\operatorname{grad}\psi. \tag{11.03.3}$$

We turn now to the analogous magnetic formulae. Each element $\mathrm{d}\boldsymbol{s}$ of a linear conductor carrying a current i makes an additive contribution

$$\mu_0 i\mathrm{d}\boldsymbol{s}/4\pi r \tag{11.03.4}$$

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* In particular Stratton, Electromagnetic Theory, McGraw-Hill 1941, hereafter referred to as S., E.T.

† S., E.T. p. 96.

to $\boldsymbol{A}$, called the *magnetic vector potential*, and $\boldsymbol{B}$ is then determined by

$$\boldsymbol{B} = \text{curl}\,\boldsymbol{A}. \qquad 11.03.5$$

The quantity μ_0 occurring in (4) is a universal constant called the *rationalized permeability of a vacuum.*

Before proceeding further it is instructive to consider the physical dimensions of the quantities occurring above in terms of the four independent dimensions length L, time T, energy U, and electric charge Q. For the present purpose it is more convenient to choose energy than mass as one of the four independent dimensions. The dimensions of the most important quantities are given in table 11.1.

TABLE 11.1

Dimensions of electromagnetic quantities

L denotes length, T time, U energy, and Q electric charge

Symbol	Name	Dimensions
Q	Electric charge	Q
i	Current	QT^{-1}
ds	Element of length	L
ids	Element of current	QLT^{-1}
ψ	Electrostatic potential	UQ^{-1}
$\boldsymbol{A}$	Magnetic vector potential	$UL^{-1}TQ^{-1}$
$\boldsymbol{E}$	Electric field strength	$UL^{-1}Q^{-1}$
$\boldsymbol{B}$	Magnetic induction	$UL^{-2}TQ^{-1}$
$\varepsilon_0\boldsymbol{E}$		QL^{-2}
$\mu_0^{-1}\boldsymbol{B}$		$QL^{-1}T^{-1}$
ε_0		$Q^2L^{-1}U^{-1}$
μ_0		$UQ^{-2}L^{-1}T^2$
μ_0^{-1}		$Q^2LT^{-2}U^{-1}$
$\varepsilon_0\mu_0$		$L^{-2}T^2$
$\varepsilon_0\boldsymbol{E}^2$		UL^{-3}
$\mu_0^{-1}\boldsymbol{B}^2$		UL^{-3}

The following points are worthy of note.

1. Inasmuch as an element of current is the analogue in a magnetic system of an element of electric charge in an electrostatic system, it is clear* that μ_0^{-1}, not μ_0, is the analogue of ε_0.
2. $(\varepsilon_0\mu_0)^{-\frac{1}{2}}$ has the dimensions of a velocity; it is well known that this quantity is equal to the speed of propagation of electromagnetic waves in a vacuum.

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* Sommerfeld, 'Electrodynamics', translated by Ramberg, Academic Press 1952 p. 21.

3. The quantities $\varepsilon_0 \boldsymbol{E}^2$ and $\mu_0^{-1} \boldsymbol{B}^2$ both have the dimensions of energy density or pressure.

The values of ε_0 and μ_0 and related quantities in the rational system are as follows:

$$\varepsilon_0 = 8.854 \times 10^{-12}\ \mathrm{C^2\ J^{-1}\ m^{-1}}$$

$$\mu_0 = 4\pi \times 10^{-7}\ \mathrm{J\ s^2\ C^{-2}\ m^{-1}} = 1.2566 \times 10^{-6}\ \mathrm{J\ s^2\ C^{-2}\ m^{-1}}$$

$$\varepsilon_0 \mu_0 = 1.1126 \times 10^{-17}\ \mathrm{s^2\ m^{-2}} = (2.9979 \times 10^8\ \mathrm{m\ s^{-1}})^{-2}.$$

§11.04 *Simplest examples of fields in a vacuum*

The formulae of the previous section are sufficient to specify completely the $\boldsymbol{E}$ field due to any given distribution of charges in a vacuum or the $\boldsymbol{B}$ field due to any given distribution of currents in a vacuum. The quantitative application of these formulae is however complicated and tedious except for systems having a high degree of symmetry. We shall consider briefly one such electrostatic system and one such magnetic system.

As the electrostatic system we choose the parallel-plate capacitor, already discussed in the previous chapter, neglecting edge effects. If charges Q and $-Q$ are distributed uniformly over the two plates each of area A at a distance d apart, then in the absence of any matter between the plates the electric field is uniform, normal to the plates, and has the value

$$|\boldsymbol{E}| = Q/\varepsilon_0 A. \qquad 11.04.1$$

As an example of a magnetic system having simple symmetry we choose a long uniform solenoid and we ignore end effects. The magnetic induction inside the empty solenoid is then uniform, parallel to the axis, and has the value

$$|\boldsymbol{B}| = \mu_0 i/l \qquad 11.04.2$$

when the current is i and there is one turn per length l.

For reasons which will appear later it is instructive to rewrite (1) and (2) in somewhat different forms. We rewrite (1) as

$$\varepsilon_0 |\boldsymbol{E}| = Qd/V_\mathrm{c} \qquad 11.04.3$$

where d is the distance between the plates so that $V_\mathrm{c} = dA$ is the volume included between the plates of the capacitor. The product Qd of the charge on a plate and the distance between the plates may be called the *electric moment* of the charged capacitor. Thus according to (3) we observe that in this system with simple symmetry $\varepsilon_0 |\boldsymbol{E}|$ is equal to the *electric moment per unit volume.*

We likewise rewrite (2) in the form

$$\mu_0^{-1}|\boldsymbol{B}| = niA/V_s \qquad 11.04.4$$

where n denotes the total number of turns, A denotes the cross-section of the solenoid, and $V_s = nlA$ denotes the volume contained by the solenoid. We may regard the solenoid as an *electromagnet* and we call the product niA its *magnetic moment.* We see then according to (4) that $\mu_0^{-1}|\boldsymbol{B}|$ is equal to the *magnetic moment per unit volume* of the solenoid.

From these relations we again perceive that μ_0^{-1}, not μ_0, is the analogue of ε_0.

§11.05 *Presence of matter*

We shall now discuss briefly the effect of filling the parallel-plate capacitor and the solenoid respectively with uniform matter.

When the space between the plates of the capacitor is filled with uniform matter, this matter becomes electrically polarized as a result of the field due to the charges on the plates. The *electric polarization* $\boldsymbol{P}$ is defined as the electric moment per unit volume induced in the matter. Owing to the symmetry of the system under consideration $\boldsymbol{P}$ is in this case uniform and normal to the plates. It is not difficult to see what will be the resultant effect on the field $\boldsymbol{E}$. We interpreted formula (11.04.3) to mean that $\varepsilon_0|\boldsymbol{E}|$ is equal to the *electric moment per unit volume* of the charged capacitor. It is evident that $\varepsilon_0|\boldsymbol{E}|$ will now be equal to the resultant electric moment per unit volume due partly to the charges $\pm Q$ on the plates and partly to the polarization of the matter between the plates. Thus in place of (11.04.3) we shall have

$$\varepsilon_0|\boldsymbol{E}| = Qd/V_c - |\boldsymbol{P}| \qquad 11.05.1$$

or

$$\varepsilon_0|\boldsymbol{E}| + |\boldsymbol{P}| = Qd/V_c = Q/A. \qquad 11.05.2$$

Thus $\varepsilon_0\boldsymbol{E} + \boldsymbol{P}$ is now related to the charge on the capacitor plates in precisely the same manner as $\varepsilon_0\boldsymbol{E}$ was related to it when the capacitor was empty. In other systems having lower symmetry the situation is less simple because $\boldsymbol{E}$ and $\boldsymbol{P}$ vary from place to place. The composite vector $\varepsilon_0\boldsymbol{E} + \boldsymbol{P}$ still however plays an important role. It is called by the curious name *electric displacement* and is denoted by $\boldsymbol{D}$. Thus by definition

$$\boldsymbol{D} = \varepsilon_0\boldsymbol{E} + \boldsymbol{P}. \qquad 11.05.3$$

From the identity (3) it is evident that any two of the vectors $\boldsymbol{E}$, $\boldsymbol{P}$, $\boldsymbol{D}$

completely determine the remaining one. It is however a fundamental assumption of electrostatics, borne out by experiment, that at any point in a piece of matter of given composition, given temperature, and given pressure any one of the vectors $\boldsymbol{E}$, $\boldsymbol{P}$, $\boldsymbol{D}$ completely determines the other two. If moreover the matter is isotropic, then $\boldsymbol{E}$, $\boldsymbol{P}$, and $\boldsymbol{D}$ have the same direction. If then we write

$$\boldsymbol{D}=\varepsilon\boldsymbol{E} \qquad 11.05.4$$

the coefficient ε is a scalar quantity, provided the matter is isotropic. (Otherwise ε would be a tensor of rank two.) The quantity ε defined by (4) is called the *permittivity* of the matter. Its value in general depends on the composition of the matter, the temperature, the pressure, and the field strength. The ratio

$$\boldsymbol{D}/\varepsilon_0\boldsymbol{E}=\varepsilon/\varepsilon_0 \qquad 11.05.5$$

is called the *relative permittivity* or the *dielectric coefficient* or, when its value is independent of $\boldsymbol{E}$, the *dielectric constant*. It is evident from (3) that $\boldsymbol{P}$ and $\boldsymbol{D}$ have the same dimensions as $\varepsilon_0\boldsymbol{E}$, namely that of charge/area. It is likewise evident from (3) and (4) that ε has the same dimensions as ε_0, so that the *dielectric coefficient* $\varepsilon/\varepsilon_0$ is a dimensionless number.

Much of the above was implicitly assumed in the previous chapter, is moreover well known, and is seemingly irrelevant to magnetic systems. It is however convenient to have these relations before us for comparison with analogous but less understood magnetic relations.

We turn now to consider the effect of filling the uniform solenoid with uniform matter. As a result of the current in the solenoid the matter will behave as if it contained induced microscopic molecular current circuits or elementary magnets. According to (11.04.4) their contribution to $\mu_0^{-1}\boldsymbol{B}$ will be equal to the magnetic moment per unit volume; this quantity is called the *magnetization* and is denoted by $\boldsymbol{M}$. Owing to the symmetry of the solenoid, $\boldsymbol{M}$ will be parallel to the axis and so (11.04.4) has to be replaced by

$$\mu_0^{-1}|\boldsymbol{B}|=niA/V_s+|\boldsymbol{M}| \qquad 11.05.6$$

or

$$\mu_0^{-1}|\boldsymbol{B}|-|\boldsymbol{M}|=niA/V_s=i/l. \qquad 11.05.7$$

Thus the composite vector $\mu_0^{-1}\boldsymbol{B}-\boldsymbol{M}$ is now related to the current through the solenoid in precisely the same manner as $\mu_0^{-1}\boldsymbol{B}$ was related to it when the inside of the solenoid was empty. In other systems having lower symmetry the situation is less simple because $\boldsymbol{B}$ and $\boldsymbol{M}$ vary from place to place. The composite vector $\mu_0^{-1}\boldsymbol{B}-\boldsymbol{M}$ still however plays an important role. It is denoted by $\boldsymbol{H}$ and is called by the misleading name *magnetic field intensity*.

Thus

$$H=\mu_0^{-1}B-M. \qquad 11.05.8$$

The names generally used for ***E***, ***B***, ***D***, and ***H*** are extremely confusing. A few of the better authorities use better names. In particular Sommerfeld* uses the names

E	electric field strength	***B***	magnetic field strength
D	electric excitation	***H***	magnetic excitation

while Stratton† uses the names

E	electric force vector	***B***	magnetic force vector
D	electric derived vector	***H***	magnetic derived vector.

From the identity (8) it is evident that any two of the vectors ***B***, ***M***, ***H*** completely determine the remaining one. It is however a fundamental assumption of electromagnetic theory that at any point in a piece of matter of given composition, given temperature, and given pressure any one of the vectors ***B***, ***M***, ***H*** completely determines the other two. The phenomenon known as *hysteresis* contradicts the assumption; such phenomena are here expressly excluded from consideration. With this proviso we write

$$H=\mu^{-1}B \qquad 11.05.9$$

and the coefficient μ is called the *permeability* of the matter. Provided the matter is isotropic μ is a scalar. (Otherwise μ would be a tensor of rank two.) The value of μ in general depends on the composition, the temperature, the pressure, and the field strength. The ratio μ/μ_0 is called the *relative permeability* of the substance and is denoted by μ_r.

§11.06 *Electric and magnetic work*

Having completed our elementary review of the physical significance of the vectors ***E***, ***D*** and ***B***, ***H*** we shall quote without proof general formulae for electric and magnetic work.

We first consider an electrostatic system consisting of charged conductors and dielectrics. For any infinitesimal change in the system, produced by moving either an electric charge or a conductor or a dielectric, the electric work w done on the system is given by‡

$$w=\int \mathrm{d}V\,\boldsymbol{E}\,\mathrm{d}\boldsymbol{D} \qquad 11.06.1$$

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* Sommerfeld, 'Electrodynamics', translated by Ramberg, Academic Press 1952 Part 1 § 2.

† S., E.T. p. 12.

‡ S., E.T. p. 108.

where $\mathrm{d}\boldsymbol{D}$ denotes the increment of $\boldsymbol{D}$ in the element of volume $\mathrm{d}V$ and the integration extends over all space, or that part of space where the electric field does not vanish.

In the simplest case of a parallel-plate capacitor containing a uniform dielectric, if we neglect edge effects, $\boldsymbol{E}$ and $\boldsymbol{D}$ vanish outside the capacitor, while between the plates they are uniform having the values

$$|\boldsymbol{D}| = Q/A \qquad 11.06.2$$

$$|\boldsymbol{E}| = Q/\varepsilon A \qquad 11.06.3$$

where $\pm Q$ denotes the charge on either plate of area A. If then d denotes the distance between the plates and V_c the volume contained between them, formula (1) reduces to

$$w = V_c Q \mathrm{d}Q/\varepsilon A^2 = (Qd/\varepsilon A)\mathrm{d}Q \qquad 11.06.4$$

in agreement with formula (10.04.2).

We turn now to a magnetic system consisting of current circuits and magnetic matter, concerning which our only restrictive assumption is the absence of hysteresis. For any infinitesimal change in the system either by changing the current in any circuit or by moving any conductor carrying a current, the magnetic work done on the system is*

$$w = \int \mathrm{d}V \boldsymbol{H} \mathrm{d}\boldsymbol{B} \qquad 11.06.5$$

where $\mathrm{d}\boldsymbol{B}$ is the increment of $\boldsymbol{B}$ in the element of volume $\mathrm{d}V$ and the integration extends over all space, or that part of space where the magnetic field does not vanish.

Since we have been at pains to emphasize that $\boldsymbol{B}$ is the analogue of the force vector $\boldsymbol{E}$, while $\boldsymbol{H}$ is the analogue of the derived vector $\boldsymbol{D}$, the reader may justifiably express surprise that formula (5) contains as integrand $\boldsymbol{H}\mathrm{d}\boldsymbol{B}$, not $\boldsymbol{B}\mathrm{d}\boldsymbol{H}$. The explanation of this paradox is that the analogy must not be pushed too far, because, whereas the electrostatic energy due to fixed charges is potential energy, the magnetic energy due to electric currents is kinetic energy. More precisely* while the Hamiltonian contains as integrands $\boldsymbol{E}\mathrm{d}\boldsymbol{D}$ and $\boldsymbol{H}\mathrm{d}\boldsymbol{B}$, the Lagrangian contains as integrands $-\boldsymbol{E}\mathrm{d}\boldsymbol{D}$ and $\boldsymbol{B}\mathrm{d}\boldsymbol{H}$.

In the simplest case of a long solenoid filled with a uniform isotropic substance, if we neglect end effects, $\boldsymbol{B}$ and $\boldsymbol{H}$ vanish outside the solenoid,

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* Guggenheim, Proc. Roy. Soc. A 1936 **155** 63; Broer, Physica 1946 **12** 49.

while inside they are uniform having the values

$$|\boldsymbol{H}| = i/l \qquad 11.06.6$$

$$|\boldsymbol{B}| = \mu i/l \qquad 11.06.7$$

where i denotes the current and l the length per turn. If then V_s denotes the internal volume of the solenoid, L its length, A its cross-section, and n the total number of turns, formula (5) becomes

$$w = V_s(i/l)\mathrm{d}(\mu i)/l = (A/L)n^2 i\mathrm{d}(\mu i). \qquad 11.06.8$$

§11.07 *Formula for Helmholtz function*

Once we know the general formula for magnetic work it is, as already mentioned in §11.01, a straightforward matter to write down thermodynamic formulae of general validity. For the sake of brevity and simplicity we shall neglect changes of volume whether due to change of temperature (expansivity) or to change of pressure (compressibility) or change of magnetic field (*magnetostriction*). The formulae may be applied to solid and liquid phases at constant pressure as an approximation.

Consider now a system consisting of linear conductors and magnetic matter and suppose the currents gradually increased from zero to final values corresponding to final values of $\boldsymbol{B}$ and $\boldsymbol{H}$ at each point of the system. Then the magnetic work w done on the system when the field is thus built up is

$$w = \int \mathrm{d}V \int_0^{\boldsymbol{B}} \boldsymbol{H}\,\mathrm{d}\boldsymbol{B} \qquad 11.07.1$$

where the first integration extends over all space. The second integral will depend on the relation between $\boldsymbol{B}$ and $\boldsymbol{H}$ which in turn depends on the temperature at each stage. Let us now specify that the path of integration shall be isothermal. Then the work w is equal to the increase in the Helmholtz function $\mathcal{A}$ of the system. We accordingly have

$$\mathcal{A} = \mathcal{A}^0 + \int \mathrm{d}V \underset{(T\ \text{const.})}{\int_0^{\boldsymbol{B}}} \boldsymbol{H}\,\mathrm{d}\boldsymbol{B} \qquad 11.07.2$$

where the superscript ^{0} denotes the value when $\boldsymbol{B}$ is everywhere zero, that is to say when no currents are flowing.

In the simplest case of a uniform field, as when a long solenoid of volume V is filled with a uniform substance, (2) can be written as

$$(\mathcal{A} - \mathcal{A}^0)/V = \underset{(T\ \text{const.})}{\int_0^{\boldsymbol{B}}} \boldsymbol{H}\,\mathrm{d}\boldsymbol{B} = \underset{(T\ \text{const.})}{\int_0^{\boldsymbol{B}}} \mu^{-1}\boldsymbol{B}\mathrm{d}\boldsymbol{B}. \qquad 11.07.3$$

§11.08 *Other thermodynamic functions*

From the formula for the Helmholtz function we can immediately derive formulae for the entropy S and the total energy U by differentation with respect to T. For the sake of brevity and simplicity we shall confine ourselves to the formulae valid in a region of volume V where composition and field are uniform. Using the superscript ^{0} to denote values of a function when $\boldsymbol{B}$ is zero, we derive from (11.07.3)

$$\frac{S-S^0}{V} = -\frac{\partial}{\partial T}\underset{(T\ \text{const.})}{\int_0^{\boldsymbol{B}}} \boldsymbol{H}\,\mathrm{d}\boldsymbol{B} = -\underset{(T\ \text{const.})}{\int_0^{\boldsymbol{B}}} \frac{\partial \boldsymbol{H}}{\partial T}\,\mathrm{d}\boldsymbol{B}$$

$$= -\underset{(T\ \text{const.})}{\int_0^{\boldsymbol{B}}} \frac{\partial(1/\mu)}{\partial T}\,\boldsymbol{B}\,\mathrm{d}\boldsymbol{B} \qquad 11.08.1$$

$$\frac{U-U^0}{V} = \underset{(T\ \text{const.})}{\int_0^{\boldsymbol{B}}} \left\{\frac{1}{\mu} - T\frac{\partial(1/\mu)}{\partial T}\right\} \boldsymbol{B}\,\mathrm{d}\boldsymbol{B}. \qquad 11.08.2$$

We can introduce other characteristic functions in particular $\mathcal{J}$ defined by

$$\mathcal{J}(T, \boldsymbol{H}) = \mathcal{F} - \int \mathrm{d}V\,\boldsymbol{H}\boldsymbol{B} = \mathcal{F}^0 - \int \mathrm{d}V \int_0^{\boldsymbol{H}} \boldsymbol{B}\,\mathrm{d}\boldsymbol{H}. \qquad 11.08.3$$

In the absence of permanent magnets, when $\boldsymbol{B}=0$ implies $\boldsymbol{H}=0$ throughout space, $\mathcal{J}$ has the property

$$\mathrm{d}\mathcal{J} = -S\,\mathrm{d}T - \int_0^{\boldsymbol{H}} \mathrm{d}V\,\boldsymbol{B}\,\mathrm{d}\boldsymbol{H}. \qquad 11.08.4$$

From (4) we derive

$$(\partial S/\partial \boldsymbol{H})_T = \int \mathrm{d}V (\partial \boldsymbol{B}/\partial T)_{\boldsymbol{H}} \qquad 11.08.5$$

and consequently

$$S = S^0 + \int \mathrm{d}V \underset{(T\ \text{const.})}{\int_0^{\boldsymbol{H}}} (\partial \boldsymbol{B}/\partial T)_{\boldsymbol{H}}\,\mathrm{d}\boldsymbol{H} \qquad 11.08.6$$

or in the case of a uniform field

$$(S-S^0)/V = \underset{(T\ \text{const.})}{\int_0^{\boldsymbol{H}}} (\partial \boldsymbol{B}/\partial T)_{\boldsymbol{H}}\,\mathrm{d}\boldsymbol{H} = \underset{(T\ \text{const.})}{\int_0^{\boldsymbol{H}}} (\partial \mu/\partial T)\boldsymbol{H}\,\mathrm{d}\boldsymbol{H}. \qquad 11.08.7$$

At first sight formulae (1) and (7) may seem to disagree but in fact their equivalence follows from

$$-\underset{(T\text{ const.})}{\int_0^{\boldsymbol{H}}}(\partial \boldsymbol{B}/\partial T)_{\boldsymbol{H}}\mathrm{d}\boldsymbol{H}=-\underset{(T\text{ const.})}{\int_0^{\boldsymbol{B}}}(\partial \boldsymbol{B}/\partial T)_{\boldsymbol{H}}(\partial \boldsymbol{H}/\partial \boldsymbol{B})_T\mathrm{d}\boldsymbol{B}=\underset{(T\text{ const.})}{\int_0^{\boldsymbol{B}}}(\partial \boldsymbol{H}/\partial T)_{\boldsymbol{B}}\mathrm{d}\boldsymbol{B}. \qquad 11.08.8$$

§11.09 *Case of linear induction*

Hitherto we have imposed no restriction on the relation between $\boldsymbol{H}$ and $\boldsymbol{B}$. The permeability μ was defined by

$$\mu=\boldsymbol{B}/\boldsymbol{H} \qquad 11.09.1$$

and in general μ depends on $\boldsymbol{B}$ (or $\boldsymbol{H}$) as well as on the temperature. For most materials, other than those exhibiting hysteresis, at the field strengths ordinarily used in the laboratory and at ordinary temperatures, it is found that μ is, at a given temperature, independent of $\boldsymbol{B}$. Under these conditions the integrations in the formulae of the previous two sections can be performed explicitly. Thus formulae (11.07.3), (11.08.1), and (11.08.2) reduce respectively to

$$(\mathcal{F}-\mathcal{F}^0)/V=\tfrac{1}{2}\boldsymbol{B}^2/\mu=\tfrac{1}{2}\boldsymbol{H}\boldsymbol{B}=\tfrac{1}{2}\mu\boldsymbol{H}^2 \qquad 11.09.2$$

$$(S-S^0)/V=\tfrac{1}{2}\boldsymbol{B}^2(\mathrm{d}\mu/\mathrm{d}T)/\mu^2=\tfrac{1}{2}\boldsymbol{H}^2\,\mathrm{d}\mu/\mathrm{d}T \qquad 11.09.3$$

$$(U-U^0)/V=\tfrac{1}{2}\boldsymbol{H}^2(\mu+T\,\mathrm{d}\mu/\mathrm{d}T). \qquad 11.09.4$$

Although a variation of μ with $\boldsymbol{B}$ at constant temperature is the exception, it does occur especially at low temperatures. In particular this phenomenon of *magnetic saturation* has been observed for hydrated gadolinium sulphate.* The formulae of the present section are then not applicable.

§11.10 *Specimen in uniform external field*

The relations developed so far involve integration over all space or that part of space where the field does not vanish. These integrations are usually too complicated to be practicable except in the case of a long solenoid completely filled with a uniform material. Unfortunately this example is of little practical interest. The experimenter is more interested in the behaviour of a specimen of matter introduced into a magnetic field which was uniform before the introduction of the specimen. We shall therefore transform our formulae to describe the behaviour of a specimen of magnetic material in a magnetic field which before the introduction of the specimen was uniform and of magnitude defined by $\boldsymbol{B}=\boldsymbol{B}_{\mathrm{e}}$. We call this the external

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* Woltjer and Onnes, Comm. Phys. Lab. Leiden 1923 no. 167c.

field. In contrast to $\boldsymbol{B}_\mathrm{e}$ the force vector (induction) of the uniform field before the specimen was introduced, we continue to use $\boldsymbol{B}$, $\boldsymbol{H}$, $\boldsymbol{M}$ to refer to the state with the specimen present. $\boldsymbol{M}$ of course vanishes outside the specimen. We define $\boldsymbol{H}_\mathrm{e}$, $\boldsymbol{B}_\mathrm{i}$, $\boldsymbol{H}_\mathrm{i}$, respectively by

$$\boldsymbol{B}_\mathrm{e}=\mu_0\boldsymbol{H}_\mathrm{e} \qquad 11.10.1$$

$$\boldsymbol{B}=\boldsymbol{B}_\mathrm{e}+\boldsymbol{B}_\mathrm{i}=\mu_0(\boldsymbol{H}_\mathrm{e}+\boldsymbol{H}_\mathrm{i}+\boldsymbol{M}). \qquad 11.10.2$$

By virtue of Maxwell's electromagnetic equations the following conditions are obeyed

$$\operatorname{div}\boldsymbol{B}=0 \qquad \operatorname{div}\boldsymbol{B}_\mathrm{e}=0 \qquad \operatorname{div}\boldsymbol{B}_\mathrm{i}=0 \qquad 11.10.3$$

$$\operatorname{curl}\boldsymbol{H}_\mathrm{i}=0 \qquad \operatorname{curl}(\mathrm{d}\boldsymbol{H}_\mathrm{i})=0. \qquad 11.10.4$$

We now have

$$\begin{aligned}
&\int \mathrm{d}V\boldsymbol{H}\mathrm{d}\boldsymbol{B}-\int \mathrm{d}V\boldsymbol{H}_\mathrm{e}\mathrm{d}\boldsymbol{B}_\mathrm{e}\\
&=\int \mathrm{d}V\boldsymbol{H}_\mathrm{i}\mathrm{d}\boldsymbol{B}+\int \mathrm{d}V\boldsymbol{H}_\mathrm{e}\mathrm{d}\boldsymbol{B}_\mathrm{i}\\
&=\int \mathrm{d}V\boldsymbol{H}_\mathrm{i}\mathrm{d}\boldsymbol{B}+\int \mathrm{d}V\boldsymbol{H}_\mathrm{e}\mu_0\mathrm{d}\boldsymbol{H}_\mathrm{i}+\int \mathrm{d}V\boldsymbol{H}_\mathrm{e}\mu_0\mathrm{d}\boldsymbol{M}\\
&=\int \mathrm{d}V\boldsymbol{H}_\mathrm{i}\mathrm{d}\boldsymbol{B}+\int \mathrm{d}V\boldsymbol{B}_\mathrm{e}\mathrm{d}\boldsymbol{H}_\mathrm{i}+\int \mathrm{d}V\boldsymbol{B}_\mathrm{e}\mathrm{d}\boldsymbol{M}. \qquad 11.10.5
\end{aligned}$$

But as a consequence of (3) and (4)

$$\int \mathrm{d}V\boldsymbol{H}_\mathrm{i}\mathrm{d}\boldsymbol{B}=0 \qquad \int \mathrm{d}V\boldsymbol{B}_\mathrm{e}\mathrm{d}\boldsymbol{H}_\mathrm{i}=0. \qquad 11.10.6$$

Using (6) in (5) we obtain

$$\int \mathrm{d}V\boldsymbol{H}\mathrm{d}\boldsymbol{B}-\int \mathrm{d}V\boldsymbol{H}_\mathrm{e}\mathrm{d}\boldsymbol{B}_\mathrm{e}=\int \mathrm{d}V\boldsymbol{B}_\mathrm{e}\mathrm{d}\boldsymbol{M}. \qquad 11.10.7$$

This relation and its elegant derivation are due to Casimir.*

If we integrate (7) at constant temperature the left side is the Helmholtz function with the specimen present less the Helmholtz function with the specimen absent. We call this the Helmholtz function of the interaction between the external field and the specimen and we use the superscript $^\mathrm{i}$ to denote this. We have then

$$\mathcal{F}^\mathrm{i}=\int \mathrm{d}V\underset{(T\text{ const.})}{\int}\boldsymbol{B}_\mathrm{e}\mathrm{d}\boldsymbol{M}=\underset{(T\text{ const.})}{\int}\boldsymbol{B}_\mathrm{e}\mathrm{d}\boldsymbol{m} \qquad 11.10.8$$

where $\boldsymbol{m}=\int\mathrm{d}V\boldsymbol{M}$ is the magnetic moment of the specimen.

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* Casimir, private communication, 1951; Heine, Proc. Cambridge Phil. Soc. 1955 **52** 546.

§11.11 *Other thermodynamic functions*

It is clear from (11.10.8) that $\mathcal{F}^{\mathrm{i}}$ is the characteristic function of interaction for the independent variables T, $\boldsymbol{m}$. For most purposes a more useful function is the characteristic function of interaction for the independent variables T, $\boldsymbol{B}_{\mathrm{e}}$ denoted by $\mathcal{G}^{\mathrm{i}}$ and defined by

$$\mathcal{G}^{\mathrm{i}}=\mathcal{F}-\boldsymbol{B}_{\mathrm{e}}\boldsymbol{m} \qquad 11.11.1$$

and obeying the relation

$$\mathrm{d}\mathcal{G}^{\mathrm{i}}=-S^{\mathrm{i}}\mathrm{d}T-\boldsymbol{m}\mathrm{d}\boldsymbol{B}_{\mathrm{e}}. \qquad 11.11.2$$

From (2) we derive the Maxwell-type relation

$$(\partial S^{\mathrm{i}}/\partial \boldsymbol{B}_{\mathrm{e}})_T=(\partial \boldsymbol{m}/\partial T)_{\boldsymbol{B}_{\mathrm{e}}} \qquad 11.11.3$$

and consequently

$$S^{\mathrm{i}}=\underset{(T\ \text{const.})}{\int_0^{\boldsymbol{B}_{\mathrm{e}}}}(\partial \boldsymbol{m}/\partial T)_{\boldsymbol{B}_{\mathrm{e}}}\mathrm{d}\boldsymbol{B}_{\mathrm{e}}. \qquad 11.11.4$$

§11.12 *Specimens of simple shape*

The relations containing $\boldsymbol{B}_{\mathrm{e}}$ and $\boldsymbol{M}$, while formally correct, are not of much use unless we know the relationship between $\boldsymbol{B}_{\mathrm{e}}$ and $\boldsymbol{M}$. This relationship is complicated unless the magnetic specimen has the shape of a spheroid having its axis of symmetry parallel to the external field $\boldsymbol{B}_{\mathrm{e}}$. For a spheroidal specimen with semi-axes a, b, b the vectors $\boldsymbol{B}_{\mathrm{e}}$, $\boldsymbol{B}$, $\boldsymbol{M}$ are parallel throughout the specimen and obey the linear relation

$$\boldsymbol{B}_{\mathrm{e}}/\boldsymbol{B}=\{\mu_0+D(\mu-\mu_0)\}/\mu \qquad 11.12.1$$

where D is a constant determined by the ratio b/a. It has the curious name *demagnetizing coefficient.*

When $a/b\to 0$ so that the specimen becomes a circular disc with its plane normal to the field

$$D=1 \qquad \boldsymbol{B}/\boldsymbol{B}_{\mathrm{e}}=1 \qquad \text{(circular disc).} \qquad 11.12.2$$

When $b/a\to 0$ so that the specimen has the shape of a needle parallel to the field

$$D=0 \qquad \boldsymbol{B}/\boldsymbol{B}_{\mathrm{e}}=\mu/\mu_0 \qquad \text{(needle).} \qquad 11.12.3$$

When $b=a$ so that the specimen is spherical

$$D=\tfrac{1}{3}\boldsymbol{B}/\boldsymbol{B}_{\mathrm{e}}=3\mu/(2\mu_0+\mu) \qquad \text{(sphere).} \qquad 11.12.4$$

From (11.05.8) and (11.05.9) we deduce

$$\boldsymbol{M}=\boldsymbol{B}(1/\mu_0-1/\mu). \qquad 11.12.5$$

Combining (5) with (1) we obtain

$$\boldsymbol{B}_e/\mu_0\boldsymbol{M}=\mu_0/(\mu-\mu_0)+D. \qquad 11.12.6$$

§11.13 *Diamagnetic, paramagnetic, and ferromagnetic substances*

Substances are divided into three classes according to their magnetic properties. These have the names *diamagnetic*, *paramagnetic*, and *ferromagnetic*.

In a *diamagnetic* substance μ has a constant value less than μ_0, independent of the field strength and of the temperature. For such a substance there is no magnetic term in the entropy and consequently there is no distinction between the energy and the Helmholtz function. Thus the thermodynamics of diamagnetic substances is trivial.

In a *paramagnetic* substance μ has a value greater than μ_0 and varying with the temperature. The value of μ also depends on the field, but usually varies but little with the field except in high fields or at low temperatures. Paramagnetic substances form the class to which the application of thermodynamics is most interesting and useful. The remaining sections of this chapter will be devoted almost entirely to paramagnetic substances.

A characteristic of *ferromagnetic* substances is the occurrence of *hysteresis*. This means that $\boldsymbol{M}$ is not a single-valued function of the field. When the field is varied the changes in magnetization are usually not reversible. The application of thermodynamics is accordingly difficult. Such attempts as have been made to apply thermodynamics to ferromagnetic substances are still controversial and nothing further will be said of them. Our only remarks concerning ferromagnetic substances will be of a general qualitative nature.

In ferromagnetic substances μ is greater than μ_0 and usually considerably greater than in paramagnetic substances. There can even be magnetization in the absence of any external field. This is called *permanent magnetization* or *remanent magnetization.*

When the temperature of a ferromagnetic substance is raised, the substance eventually becomes paramagnetic. The temperature at which this change occurs is called the *Curie temperature*. The change is a transition of higher order as defined in chapter 6. Thus the Curie temperature is a lambda point, in fact the first example of a lambda point to be discovered.

§11.14 *Simple paramagnetic behaviour*

We shall describe in some detail the behaviour of those paramagnetic substances whose magnetic properties are entirely due to electron spin. The behaviour of the larger class whose magnetic properties are due, partly or entirely, to orbital angular momentum is qualitatively similar but quantitatively more complicated. A description of these will not be attempted here as it would require too much space. The reader interested will have to turn to a more specialized source of information.*

The fundamental unit of magnetic moment in electron theory is *Bohr's magneton* and all magnetic moments will be expressed in terms of this unit. Bohr's magneton is denoted by β and is defined by

$$\beta = eh/4\pi m_e \qquad 11.14.1$$

where $-e$ denotes the charge and m_e the mass of an electron while h, as usual, denotes the Planck constant. If we multiply (1) by the Avogadro constant L, we obtain the corresponding proper unit

$$L\beta = Fh/4\pi m_e \qquad 11.14.2$$

where F denotes the Faraday constant. Inserting the numerical values

$$F = 9.649 \times 10^4 \text{ C mole}^{-1}$$

$$m_e = 9.109 \times 10^{-31} \text{ kg}$$

$$h = 6.626 \times 10^{-34} \text{ kg m}^2 \text{ s}^{-1}$$

we obtain

$$L\beta = 5.586 \text{ A m}^2 \text{ mole}^{-1}. \qquad 11.14.3$$

Correspondingly for β we have

$$\begin{aligned}\beta &= 5.586 \times 1.6601 \times 10^{-24} \text{ A m}^2 \\ &= 9.272 \times 10^{-24} \text{ A m}^2. \qquad 11.14.4\end{aligned}$$

Following standard spectroscopic notation we shall denote the resultant spin quantum number by S, so that the multiplicity is $2S+1$. Examples of values of S for some typical paramagnetic ions of transition elements are given in table 11.2. The first and last ions in the table, having $S=0$, are diamagnetic.

We now consider a substance such as ammonium ferric alum $NH_4Fe(SO_4)_2{\cdot}12H_2O$ each molecule of which contains a considerable number of atoms, in this example 52, only one of which, in this case Fe, is paramagnetic. In such a substance the paramagnetic ions, in this case

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* Van Vleck, Electric and Magnetic Susceptibilities, Clarendon Press 1932 p. 259.

Fe^{3+}, may usually be considered as mutually independent, each making its own contribution to the paramagnetism of the substance. We shall denote the proper volume as usual by V_m, this being the volume which contains L paramagnetic ions.

TABLE 11.2

Multiplicities of typical paramagnetic ions of transition elements

Ions	Number of 3d electrons	S	$2S+1$
Sc^{3+}	0	0	1
Sc^{2+}, Ti^{3+}, V^{4+}	1	½	2
Ti^{2+}, V^{3+}	2	1	3
V^{2+}, Cr^{3+}	3	1½	4
Cr^{2+}, Mn^{3+}	4	2	5
Mn^{2+}, Fe^{3+}	5	2½	6
Fe^{2+}	6	2	5
Co^{2+}	7	1½	4
Ni^{2+}	8	1	3
Cu^{2+}	9	½	2
Cu^{+}, Zn^{2+}	10	0	1

We consider a small spherical specimen of such a substance placed in a uniform external magnetic field with induction $\boldsymbol{B}_e$. Then for the independent variables T, $\boldsymbol{B}_e$ the characteristic function $\mathcal{J}^i$ of the interaction between the specimen and the field is given by

$$\mathcal{J}^i \frac{V_m}{V_s} = -RT \ln \frac{\sinh\{(2S+1)L\beta\boldsymbol{B}_e/RT\}}{\sinh\{L\beta\boldsymbol{B}_e/RT\}} \qquad 11.14.5$$

where V_s denotes the volume of the specimen. Formula (5) is essentially due* to Brillouin.

From formula (5) we can derive all the thermodynamic formulae relating to the magnetic properties of the specimen. The magnetic moment $\boldsymbol{m}$ of the specimen is determined by

$$\boldsymbol{m} = -\partial\mathcal{J}^i/\partial\boldsymbol{B}_e \qquad 11.14.6$$

and the magnetization $\boldsymbol{M}$ by

$$\boldsymbol{M}V_s = -\partial\mathcal{J}^i/\partial\boldsymbol{B}_e. \qquad 11.14.7$$

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* Van Vleck, Electric and Magnetic Susceptibilities, Clarendon Press 1932; Stoner, Magnetism and Matter 1934.

From (5) and (7) we derive

$$\boldsymbol{M}V_{\mathrm{m}}=(2S+1)L\beta\coth\{(2S+1)L\beta\boldsymbol{B}_{\mathrm{e}}/RT\}-L\beta\coth\{L\beta\boldsymbol{B}_{\mathrm{e}}/RT\}. \tag{11.14.8}$$

We shall study the particular case $S=\frac{1}{2}$ before continuing with the general case. When $S=\frac{1}{2}$, formula (8) reduces to the simple form

$$\boldsymbol{M}V_{\mathrm{m}}=L\beta\tanh\{L\beta\boldsymbol{B}_{\mathrm{e}}/RT\}. \tag{11.14.9}$$

We see at once that for sufficiently small field strengths we may replace (9) by the approximation

$$\boldsymbol{M}V_{\mathrm{m}}=(L\beta)^2\boldsymbol{B}_{\mathrm{e}}/RT \qquad (L\beta\boldsymbol{B}_{\mathrm{e}}\ll RT) \tag{11.14.10}$$

so that $\boldsymbol{M}$ is directly proportional to $\boldsymbol{B}_{\mathrm{e}}$ and inversely proportional to T. This behaviour is known as *Curie's law*. At the opposite extreme of sufficiently high values of $\boldsymbol{B}_{\mathrm{e}}$ we may replace (9) by the approximation

$$\boldsymbol{M}V_{\mathrm{m}}=L\beta \qquad (L\beta\boldsymbol{B}_{\mathrm{e}}\gg RT) \tag{11.14.11}$$

so that $\boldsymbol{M}$ is independent of $\boldsymbol{B}_{\mathrm{e}}$ and of T. This behaviour is called *magnetic saturation*. We shall soon see that for all values of S Curie's law holds in sufficiently low fields and saturation occurs in sufficiently high fields.

We now return to the general formula (5) and consider its simplification in the two extremes of large and of small $\boldsymbol{B}_{\mathrm{e}}$. Considering first large values of $\boldsymbol{B}_{\mathrm{e}}$ we replace each sinh by $\frac{1}{2}$ exp and obtain immediately

$$\mathscr{A}^{\mathrm{i}}V_{\mathrm{m}}/V_{\mathrm{s}}=-2SL\beta\boldsymbol{B}_{\mathrm{e}} \qquad (L\beta\boldsymbol{B}_{\mathrm{e}}\gg RT). \tag{11.14.12}$$

From (7) and (12) we derive

$$\boldsymbol{M}V_{\mathrm{m}}=2SL\beta \qquad (L\beta\boldsymbol{B}_{\mathrm{e}}\gg RT) \tag{11.14.13}$$

representing saturation.

We turn now to the opposite extreme of small $\boldsymbol{B}_{\mathrm{e}}$. We expand each sinh as a power series retaining the first two terms. We then expand the logarithm, again retaining the first two terms. We thus obtain

$$\mathscr{A}^{\mathrm{i}}V_{\mathrm{m}}/V_{\mathrm{s}}=-RT\ln(2S+1)-4S(S+1)(L\beta\boldsymbol{B}_{\mathrm{e}})^2/6RT \qquad (L\beta\boldsymbol{B}_{\mathrm{e}}\ll RT). \tag{11.14.14}$$

From (7) and (14) we derive

$$\boldsymbol{M}V_{\mathrm{m}}=4S(S+1)(L\beta)^2\boldsymbol{B}_{\mathrm{e}}/3RT \qquad (L\beta\boldsymbol{B}_{\mathrm{e}}\ll RT) \tag{11.14.15}$$

so that $\boldsymbol{M}$ is directly proportional to $\boldsymbol{B}_{\mathrm{e}}$ and inversely proportional to T in accordance with *Curie's law*.

Formula (15) has been verified experimentally for numerous substances. The more general theoretical relation (8) between $\boldsymbol{M}$ and $\boldsymbol{B}_{\mathrm{e}}$ extending from the extreme of Curie's law to the opposite extreme of saturation has been quantitatively verified* for hydrated gadolinium sulphate, in which the paramagnetic Gd^{3+} ion is in an $^8\mathrm{S}$ state with $S=3\frac{1}{2}$.

§11.15 *Entropy of simple paramagnetic substances*

We continue to restrict our discussion to substances whose paramagnetism is due entirely to electron spin. The behaviour of other paramagnetic substances is qualitatively similar but more complicated.

By differentiating (11.14.5) with respect to T we can obtain a general formula for S^{i}, the entropy of interaction between the field and the specimen. For the sake of brevity we shall however confine ourselves to the two extreme cases of $\boldsymbol{B}_{\mathrm{e}}$ large and of $\boldsymbol{B}_{\mathrm{e}}$ small.

At magnetic saturation according to (11.14.12) the function $\mathcal{A}^{\mathrm{i}}$ is independent of the temperature and the entropy S^{i} vanishes.

Under the opposite conditions of small field we derive from (11.14.14)

$$\frac{S^{\mathrm{i}}}{R}\frac{V_{\mathrm{m}}}{V_{\mathrm{s}}}=\ln(2S+1)-\frac{4S(S+1)}{6}\left(\frac{L\beta\boldsymbol{B}_{\mathrm{e}}}{RT}\right)^2 \qquad (L\beta\boldsymbol{B}_{\mathrm{e}}\ll RT). \qquad 11.15.1$$

§11.16 *Adiabatic demagnetization*

In a system whose state can be completely defined by the temperature T and the external magnetic field $\boldsymbol{B}_{\mathrm{e}}$ (all other degrees of freedom such as pressure and composition being either irrelevant or held constant), the equation for a reversible adiabatic process is

$$S(T,\boldsymbol{B}_{\mathrm{e}})=\text{const.} \qquad \text{(adiabatic).} \qquad 11.16.1$$

In a sample of a paramagnetic substance, such as ferric alum, in the temperature range 2 K to 4 K all contributions to the entropy from translational, rotational, intramolecular, and vibrational degrees of freedom are effectively zero, while any contributions from intranuclear degrees of freedom remain constant. Hence for adiabatic variations of the field $\boldsymbol{B}_{\mathrm{e}}$ we have

$$S^{\mathrm{i}}(T,\boldsymbol{B}_{\mathrm{e}})=\text{const.} \qquad \text{(adiabatic).} \qquad 11.16.2$$

Provided $\boldsymbol{B}_{\mathrm{e}}$ is not too great, we may use formula (11.15.1) for S^{i}, so that (2) leads to

$$\boldsymbol{B}_{\mathrm{e}}/T=\text{const.} \qquad \text{(adiabatic).} \qquad 11.16.3$$

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* Woltjer and Onnes, Comm. Phys. Lab. Leiden 1923 no. 167c.

Thus when the field is reduced the temperature drops proportionally. This is the principle of cooling by *adiabatic demagnetization.*

§11.17 *Unattainability of zero temperature*

By means of adiabatic demagnetization temperatures as low as 10^{-3} K have been reached. It would appear from formula (11.16.3) that by reducing the external field to zero, we should reach $T=0$ in contradiction of Nernst's heat theorem. The resolution of this paradox is that before $T=0$ is reached, usually in the region $T \approx 10^{-2}$ K, the formulae of §11.14 and §11.15 cease to be applicable. In other words, at some such temperature the substance ceases to be paramagnetic but becomes eventually either diamagnetic or ferromagnetic.

In the change from the paramagnetic to the diamagnetic or ferromagnetic state, the proper entropy in zero magnetic field is reduced by an amount

$$R \ln(2S+1). \qquad 11.17.1$$

Hence by comparison with (11.15.1), we see that the value of S^{i} for zero field falls to zero. This is in agreement with the third principle of thermodynamics as expounded in chapter 3. The reader must turn elsewhere* for details of such changes.

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* For example Debye, Ann. Phys. Lpz. 1938 **32** 85. An excellent elementary account is given by Simon, Very Low Temperatures, Science Museum Handbook 1937 No. 3 p. 58.