CHAPTER 10

ELECTROSTATIC SYSTEMS

§10.01 *Introduction*

We now propose to study the thermodynamic properties of substances in an electrostatic field. For this purpose it will suffice to consider the field in a parallel-plate capacitor neglecting any edge effect. Thus when we refer to the extensive properties of a parallel-plate capacitor of area A, we really mean the difference between those of a capacitor of area $\mathscr{A}+A$ and those of a similar capacitor of area $\mathscr{A}$, where $\mathscr{A} \gg A$.

§10.02 *Parallel-plate capacitor in vacuo*

Consider a parallel-plate capacitor of area A, the distance between the plates being d. Let the charges on the two plates be $+Q$ and $-Q$. The capacitor being in vacuo let the work required to transfer an elementary charge $\mathrm{d}Q$ from the negative plate α to the positive plate β be $(\psi^{\beta}-\psi^{\alpha})\mathrm{d}Q$. Then $\psi^{\beta}-\psi^{\alpha}$ is called the *potential difference* between the two plates and $\boldsymbol{E}=-(\psi^{\beta}-\psi^{\alpha})/d$ is called the *electric field strength* between the plates. Then the ratio ε_0 defined by

$$Qd/A(\psi^{\beta}-\psi^{\alpha})=Q/A\boldsymbol{E}=\varepsilon_0 \qquad 10.02.1$$

is a universal constant called the *rationalized permittivity of a vacuum*. The value of ε_0 is given by

$$\begin{aligned}\varepsilon_0 &= 8.854\times 10^{-12}\ \mathrm{C}^2\ \mathrm{J}^{-1}\ \mathrm{m}^{-1}\\ 4\pi\varepsilon_0 &= 1.113\times 10^{-10}\ \mathrm{C}^2\ \mathrm{J}^{-1}\ \mathrm{m}^{-1}\\ &= 1.113\times 10^{-10}\ \mathrm{A\ s\ V}^{-1}\ \mathrm{m}^{-1}\end{aligned}$$

§10.03 *Parallel-plate capacitor in fluid*

Now consider the same parallel-plate capacitor completely immersed in a homogeneous fluid. If the charges on the plates are again $+Q$ and $-Q$, and if the potential difference between the plates, defined as before, is again denoted by $\psi^\beta - \psi^\alpha$ then the ratio ε, defined by

$$Qd/A(\psi^\beta - \psi^\alpha) = Q/AE = \varepsilon \qquad 10.03.1$$

is called the *rationalized permittivity of the fluid.* The value of ε depends on the nature of the fluid, on its temperature, and possibly also on $\boldsymbol{E}$, but is independent of the size and shape of the capacitor. ε has of course the same dimensions as ε_0. The ratio $\varepsilon_r = \varepsilon/\varepsilon_0$ is called the *relative permittivity* or the *dielectric coefficient* of the fluid.

§10.04 *Work of charging a capacitor*

According to (10.03.1) we have

$$\psi^\beta - \psi^\alpha = Qd/\varepsilon A \qquad 10.04.1$$

and so the work required to bring an element of charge $\mathrm{d}Q$ from the negative plate α to the positive plate β is

$$(Qd/\varepsilon A)\mathrm{d}Q. \qquad 10.04.2$$

From (10.03.1) we have also

$$Q = A\varepsilon \boldsymbol{E} \qquad 10.04.3$$

$$\mathrm{d}Q = A\,\mathrm{d}(\varepsilon \boldsymbol{E}). \qquad 10.04.4$$

Substituting (3) and (4) into (2) we obtain for the work w required to increase the field strength from $\boldsymbol{E}$ to $\boldsymbol{E}+\mathrm{d}\boldsymbol{E}$

$$w = Ad\boldsymbol{E}\,\mathrm{d}(\varepsilon \boldsymbol{E}) = V_c \boldsymbol{E}\,\mathrm{d}(\varepsilon \boldsymbol{E}) \qquad 10.04.5$$

where V_c denotes the volume between the plates of the capacitor and is assumed independent of temperature and pressure.

Formula (5) is valid for any infinitesimal change, including in particular an adiabatic change and an isothermal change, but the dependence of $\varepsilon \boldsymbol{E}$ on $\boldsymbol{E}$ will in general not be the same in these two cases. The quantity $\varepsilon \boldsymbol{E}$ is called the *electric displacement.*

§10.05 *Characteristic functions*

If we now consider the system consisting of the whole fluid of volume V surrounding and including the capacitor, we obtain by using (10.04.5) the relations

$$\mathrm{d}U = T\mathrm{d}S - P\mathrm{d}V + V_c \boldsymbol{E}\,\mathrm{d}(\varepsilon \boldsymbol{E}) + \sum_i \mu_i \mathrm{d}n_i \qquad 10.05.1$$

$$\mathrm{d}\mathscr{F} = -S\mathrm{d}T - P\mathrm{d}V + V_\mathrm{c}\boldsymbol{E}\mathrm{d}(\varepsilon\boldsymbol{E}) + \sum_i \mu_i \mathrm{d}n_i. \qquad 10.05.2$$

Formulae (1) and (2) are the extensions of (1.28.6), (1.28.7) respectively including the extra term (10.04.5) representing the work required to change the field $\boldsymbol{E}$ between the plates of the capacitor.

We now define the characteristic function G by

$$G = U - TS + PV - V_\mathrm{c}\varepsilon\boldsymbol{E}^2. \qquad 10.05.3$$

Differentiating (3) and substituting into (1), we obtain

$$\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}P - V_\mathrm{c}\varepsilon\boldsymbol{E}\mathrm{d}\boldsymbol{E} + \sum_i \mu_i \mathrm{d}n_i. \qquad 10.05.4$$

In all the above formulae V denotes the total volume of fluid in which the capacitor is immersed and P denotes the pressure acting on the outside boundary of the fluid in which the capacitor is completely immersed. We have carefully avoided reference to any pressure within the fluid between the plates of the capacitor, for the definition of such a pressure would require special caution and its use as an independent variable would lead to more complicated formulae.

§10.06 *Analogues of Maxwell's relations*

By forming the second differential coefficients of the characteristic functions we can obtain several relations analogous to Maxwell's relations obtained in §1.47. In particular from (10.05.4) we derive

$$(\partial S/\partial \boldsymbol{E})_{T,P} = V_\mathrm{c}(\partial[\varepsilon\boldsymbol{E}]/\partial T)_{P,\boldsymbol{E}} = V_\mathrm{c}\boldsymbol{E}(\partial\varepsilon/\partial T)_{P,\boldsymbol{E}} \qquad 10.06.1$$

$$(\partial V/\partial \boldsymbol{E})_{T,P} = -V_\mathrm{c}(\partial[\varepsilon\boldsymbol{E}]/\partial P)_{T,\boldsymbol{E}} = -V_\mathrm{c}\boldsymbol{E}(\partial\varepsilon/\partial P)_{T,\boldsymbol{E}}. \qquad 10.06.2$$

This change in volume accompanying change in field strength at constant temperature and pressure is called *electrostriction.*

§10.07 *Constant permittivity. Dielectric constant*

For the sake of generality we have hitherto made no assumption concerning the dependence of the permittivity ε on the field strength $\boldsymbol{E}$. For almost all substances at field strengths met in an ordinary laboratory the permittivity ε is for a given temperature and pressure independent of the field strength. We shall from here onwards assume this to be the case. The *relative permittivity* or *dielectric coefficient* $\varepsilon_\mathrm{r} = \varepsilon/\varepsilon_0$ is then called the *dielectric constant.*

Formula (10.06.1) may now be written more simply as

$$(\partial S/\partial E)_{T,P} = V_c E(\partial \varepsilon/\partial T)_P \qquad 10.07.1$$

and the electrostriction formula (10.06.2) as

$$(\partial V/\partial E)_{T,P} = -V_c E(\partial \varepsilon/\partial P)_T . \qquad 10.07.2$$

§10.08 *Integrated formulae*

When we assume that ε is independent of E we can integrate (10.05.4) at constant T, P, n_i obtaining

$$G = G^0 - \tfrac{1}{2}\varepsilon E^2 V_c \qquad 10.08.1$$

where the superscript ^{0} denotes the value at zero field at the given temperature, pressure, and composition.

By differentiation of (1) we obtain

$$S = S^0 + \tfrac{1}{2}(\partial \varepsilon/\partial T)E^2 V_c \qquad 10.08.2$$

$$V = V^0 - \tfrac{1}{2}(\partial \varepsilon/\partial P)E^2 V_c \qquad 10.08.3$$

$$\mu_i = \mu_i^0 - \tfrac{1}{2}(\partial \varepsilon/\partial n_i)E^2 V_c \qquad 10.08.4$$

from which we deduce

$$H = H^0 + \tfrac{1}{2}\{\varepsilon + T(\partial \varepsilon/\partial T)\}E^2 V_c \qquad 10.08.5$$

$$U = U^0 + \tfrac{1}{2}\{\varepsilon + T(\partial \varepsilon/\partial T) + P(\partial \varepsilon/\partial P)\}E^2 V_c . \qquad 10.08.6$$

We must point out that the statement occurring in text-books on electricity that the energy density due to the field is $\tfrac{1}{2}\varepsilon E^2$ is false.

§10.09 *Application to perfect gas*

We shall illustrate the use of the relation (10.08.4) by its application to the simplest case of a single perfect gas.

The rationalized permittivity ε of a perfect gas is related to the rationalized permittivity ε_0 of a vacuum by

$$\varepsilon - \varepsilon_0 = (Ln/V)(\alpha + \beta/T) \qquad 10.09.1$$

where α is equal to the molecular polarizability and β is given by

$$\beta = \boldsymbol{\mu}^2/3k \qquad 10.09.2$$

where $\boldsymbol{\mu}$ is the electric moment of the molecule and k the Boltzmann constant.

Substituting (1) into (10.08.4) we obtain

$$\mu=\mu^0-\tfrac{1}{2}E^2L(\alpha+\beta/T)$$

$$=\mu^\ominus+RT\ln(nRT/P^\ominus V)-\tfrac{1}{2}E^2L(\alpha+\beta/T). \qquad 10.09.3$$

Let us now consider the equilibrium distribution of a gas between the region, denoted by the superscript $^{\mathrm{i}}$, inside a capacitor where the field strength is E and the region, denoted by the superscript $^{\mathrm{e}}$, exterior to this field. We have then

$$\mu^{\mathrm{i}}=\mu^\ominus+RT\ln(n^{\mathrm{i}}RT/V^{\mathrm{i}}P^\ominus)-\tfrac{1}{2}E^2L(\alpha+\beta/T) \qquad 10.09.4$$

$$\mu^{\mathrm{e}}=\mu^\ominus+RT\ln(n^{\mathrm{e}}RT/V^{\mathrm{e}}P^\ominus). \qquad 10.09.5$$

The equilibrium distribution is determined by

$$\mu^{\mathrm{i}}=\mu^{\mathrm{e}}. \qquad 10.09.6$$

Substituting (4) and (5) into (6), we obtain, writing c for n/V,

$$RT\ln(c^{\mathrm{i}}/c^{\mathrm{e}})-\tfrac{1}{2}E^2L(\alpha+\beta/T)=0 \qquad 10.09.7$$

or

$$c^{\mathrm{i}}/c^{\mathrm{e}}=\exp\{(\tfrac{1}{2}E^2/RT)(\alpha+\beta/T)\}. \qquad 10.09.8$$

Since α is always positive and β is either positive or zero, it follows that c is always greater inside the field than outside it. Thus every perfect gas is attracted into an electric field.