3.5. The Einstein Diffusion Equation

As a last application of the Maxwell-Boltzmann statistics to be considered in this chapter a relationship will be derived between the mobility μ and the diffusion coefficient D of ions in a gas. Consider a gas contained in a vessel with non-conducting walls.

Let there be an electric field E applied across the gas by means of charged plates outside the vessel as shown in Fig.3 and let there be $n(x)$ ions per unit volume at distance x from the end of the vessel. If the charge on each ion is q then the potential energy of an ion at x, compared with that of an ion at $x = 0$, will be

$$\epsilon(x) = -qEx$$

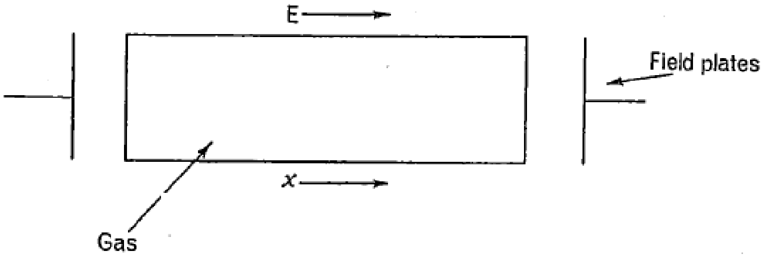

Fig. 3. Gas containing ions in electric field.

provided that the concentration *of* the ions is insufficient to affect the uniformity of the value of the electric field. Because of this energy gradient there will be a concentration gradient of ions in the gas. Using the Boltzmann factor for the relative probability that an ion will have a particular energy gives

$$\frac{n(x)}{n(0)} = e^{-\epsilon(x)/kT} = e^{qEx/kT} \qquad \textbf{3.25}$$

Where n(0) is the concentration of ions at $x = 0$ and T is the temperature of the gas.

Now, if the ions have a mobility μ, there will be an ionic drift velocity μE in the direction of the field E. There will thus be a drift current of ions across the plane at x equal to

$$j\ (\text{drift}) = n(x).\ \mu E \qquad \textbf{3.26}$$

per unit area per unit time.

Also, if D is the diffusion coefficient for the ions, there will be a diffusion current of ions across unit area at which, by definition, is

$$j\,(\text{diffusion}) = -D\frac{dn(x)}{dx} \qquad 3.27$$

per unit time in the direction of the concentration gradient. However, since in the case under discussion there can be no total current flow, there can be no total movement of ions. Thus

$$j\,(\text{drift}) + j\,(\text{diffusion}) .= 0$$

or, from equations 3.26 and 3.27,

$$n(x)\,.\,\mu E = D\frac{dn(x)}{dx} \qquad 3.28$$

Substituting for *n(x)* from equation 3.25 gives

$$\frac{dn(x)}{dx} = n(x)\,.\,\frac{qE}{kT}$$

so that equation 3.28 becomes

$$\mu = \frac{Dq}{kT}$$

or

$$\frac{\mu}{D} = \frac{q}{kT}$$

which is the Einstein Diffusion Equation.

The Canonical Ensemble

4.1. Ensembles

Up to this point the discussion has been mainly limited to these assemblies in which both the total energy and the number of systems could be considered as fixed quantity and in which there were no interactions between component systems. In order that the statistical method may be extended to a wider range of physical problems it is useful to introduce the concept of an **ensemble**. For this purpose consider a group of assemblies which all have the same volume and in which the component systems are all of the same type.

Then, depending on the considerations imposed on the assemblies, there will be a large number of distinct arrangements of the systems (i.e. microstates

4.2. The constant temperature ensemble

Because the assemblies in a canonical ensemble are defined as being all at the same temperature, it is possible to consider that neighboring assemblies within the ensemble are in thermal contact with each other. Then, when the assemblies are in a state of thermodynamic equilibrium, the complete ensemble may be considered as forming a constant temperature enclosure. The form of this constant temperature ensemble may be illustrated as in Fig. 4 where the boundaries of the assemblies fix the number of systems, N, and the volume V to be the same for each assembly. However, since these boundaries are permeable to the transfer of energy (or heat), they do not fix the energies of the assemblies-and it is the temperature T which is the same throughout the ensemble.* The energy of an assembly within the canonical ensemble may thus, theoretically, vary with time over all values from zero to the total energy of the ensemble.

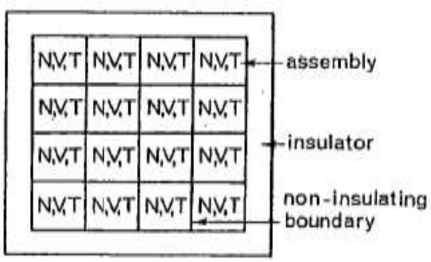

Fig.4. The canonical or constant temperature ensemble.