

## Si Conduction

The conduction of electricity in Si is quite different from the conduction in metals. Metals have an ionic structure with a vast number of conduction electrons available - one per metal atom, typically. Since there are  $\sim 10^{22}$  atoms  $\text{cm}^{-3}$  in a metal, the density of conduction electrons is very high. When a potential is placed across a metal the electrons move due to the force of the electric field and the conductivity  $\sigma$  is proportional to the electron density. The resistivity  $\rho = \frac{1}{\sigma}$  is low ( $\rho \sim 10^{-6}$  ohm-cm for a good conductor such as Cu or Al at room

temperature). Si has a diamond like structure due to the fact that Si has four valence electrons and each atom bonds to four nearest neighbors by this strong, two-electron valence bond (each atom in a Si - Si bond contributes one electron to the bond).

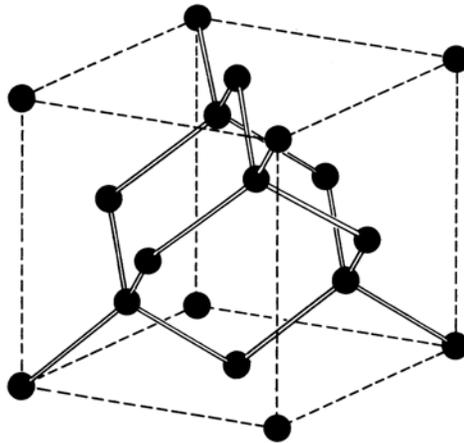


Fig. 1. The three-dimensional representation of the Si lattice (diamond-like). Each Si atom bonds covalently to the four nearest neighbors.

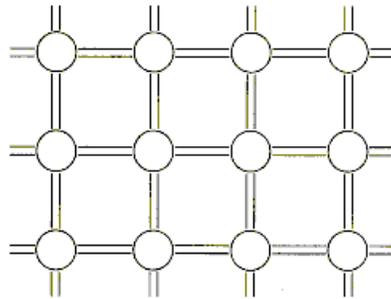


Figure 2. A two-dimensional representation of the Si lattice explicitly showing the two-electron covalent bonds.

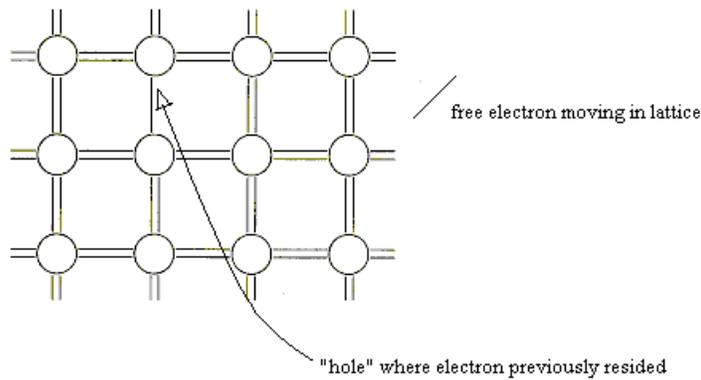


Figure 3. Two-dimensional representation of the Si lattice showing formation of an electron-hole pair.

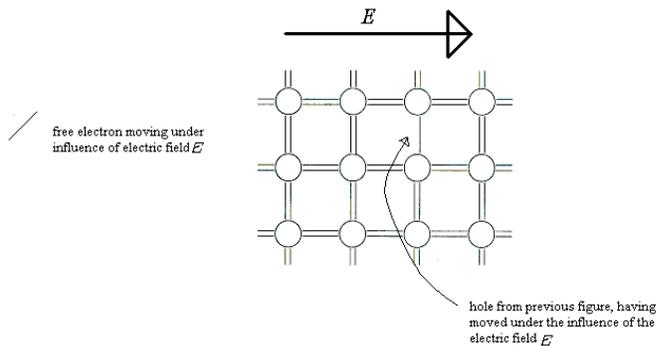


Figure 4. Schematic representation of the motion of the electron and the hole from Figure 3 moving in an applied electric field  $E$ .

At 0K essentially every valence electron is bound to two Si atoms and the resistivity of the Si is extremely high. At higher temperatures thermal jostling of the atoms occasionally will allow an electron to free itself from a bond and to wander through the crystal lattice. The vacancy left behind by the electron is called a hole, and it too can move from atom to atom. At room temperature ( $\approx 293$  K) there are about  $10^{10}$  electrons and holes  $\text{cm}^{-3}$  in pure Si and the resistivity is correspondingly high - hundreds of thousands of ohm-cm.

The motion of holes and electrons is random unless an electric field is applied to the Si. In this case a general drift is imposed on the random motion of the electrons and holes: the electrons move in the direction opposite to the electric field vector while the holes move in the same direction as the electric field. Because the density of holes and electrons in Si is vastly less than the density of electrons in a metal, the conductivity is much less than a metal and so Si is called a semiconductor. The resistivity of pure Si at room temperature is about  $3 \times 10^5$  ohm-cm, some ten orders of magnitude greater than copper and about ten orders of magnitude less than that of an excellent insulator such as  $\text{SiO}_2$  (quartz).

## Holes

Holes are somewhat curious objects at first: they are the absence of electrons but their motion represents an electric current. One way to think about holes is to imagine an electron being removed from a Si - Si bond, leaving only one electron shared between the two atoms. If an electron from a neighboring bond jumps in to fill the gap, the hole left by the absence of an electron can move from its original location to a neighboring location. In this way electrons migrate in one direction from atom to atom (they are not free, like the electron that got away) and so, effectively, a positive charge moves the other way: hole current to the right means electrons are moving from atom to atom to the left. However, for our purposes it is advantageous to treat a hole as an actual particle carrying electric charge  $+q$  and having a finite mass, and we will consider the hole to be a particle here and treat current flow in terms of the motion of the two kinds of charge carriers, holes and electrons.

## Electron-hole pairs

As we mentioned, the reason the resistivity of pure Si is so high relative to a metal is that the density of holes and electrons in Si is so small compared to a metal (in fact, holes do not exist in metals since metal atoms don't bind via a valence bond). In Si  $n_i$  is about one trillionth the density of Si atoms:  $n_i = 10^{10}$  (holes or electrons)  $\text{cm}^{-3}$  compared to  $5 \times 10^{22}$  atoms  $\text{cm}^{-3}$ . This is to be compared to a metal where the electron density is  $\sim$  atomic density because free electrons are created when the metal atoms bond together (there are no holes in metals). The reason for this is that the amount of energy required to break a bond and free an electron, creating thereby an *electron-hole pair* in Si, is about 1.1 electron-volts, or 1.1 eV. (1 electron volt is the energy acquired by an electron dropping through an electric potential of one volt which isn't much energy:  $1 \text{ eV} = 1.6 \times 10^{-19} \text{ C} \times 1 \text{ V} = 1.6 \times 10^{-19}$  joules. An angry fly stamping its foot on the floor probably uses up  $10^{-8}$  joules or around  $10^{11}$  eV). The average energy  $U$  of an electron or a hole in Si due to thermal jostling is  $U = kT$ , where  $k$  is Boltzmann's constant =  $1.38 \times 10^{-23}$  joule  $\text{deg}^{-1}$  and  $T$  is the temperature (K). At room temperature (293 K)  $U = 4 \times 10^{-21}$  joules, or 0.025 eV. Thus the average thermal energy is more than forty times smaller than the energy needed to break a bond, and, since the probability for a bond breaking is proportional to  $e^{-\frac{\text{BondEnergy}}{kT}}$ ,

relatively few are broken. The factor  $e^{-\frac{\text{BondEnergy}}{kT}}$  is the Boltzmann factor which comes from classical statistical mechanics (**Maxwell-Boltzmann Distribution**)

Si conducts because there are so many ( $5 \times 10^{22}$ ) atoms per  $\text{cm}^{-3}$  that a reasonable number ( $10^{10}$ ) of electron-hole pairs are in existence at any given time. As the temperature decreases the number of pairs also decreases and at absolute zero (0 K) Si is an insulator. Metals conduct at 0 K.

## Maxwell-Boltzmann distribution

Using classical statistical mechanics based on classical probability theory it is possible to derive a relationship between the *temperature* of an ensemble of particles such as atoms or electrons, which is a measure of the average energy of the particles, and the kinetic energy of each particle. The result is a distribution function giving the probability for finding a certain number of particles with energy between  $U$  and  $U + dU$ . The Maxwell-Boltzmann (M-B) distribution

function is  $f(U) = \frac{2}{\sqrt{\pi}} (kT)^{-3/2} \sqrt{U} e^{-\frac{U}{kT}}$  where the kinetic energy is  $U = p^2/2m$  ( $p$  is the

momentum).  $\int_0^{\infty} f(U) dU = 1$ . The shape of this distribution ( $f(U)$  plotted vs.  $U$ ) is shown in

Figure 1.

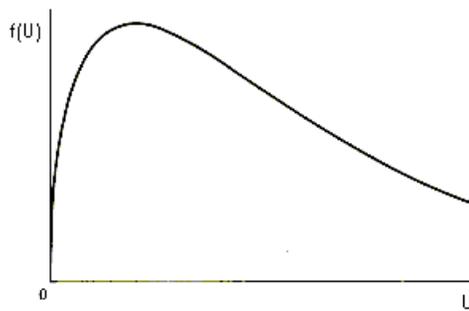


Figure 1. The distribution function  $f(U)$  plotted vs. the energy  $U$ .

For an example of the use of the M-B distribution, the average kinetic energy  $\langle U \rangle$  of a particle is found by integrating the distribution multiplied by the energy of a particle:

$$\bar{U} = \frac{2}{\sqrt{\pi}} (kT)^{-3/2} \int_0^{\infty} U \sqrt{U} e^{-\frac{U}{kT}} = \frac{3}{2} kT, \text{ thus relating average energy and temperature. The}$$

exponential factor  $e^{-\frac{\text{Energy}}{kT}}$  from the M-B distribution comes up all the time in physics; it is not exactly correct because the M-B distribution was derived before the discovery of quantum mechanics; classical probability theory isn't correct at the atomic level, but for many purposes the difference between the exact statistics (called Fermi-Dirac statistics for electrons and holes) and the M-B distribution is small.

## **Single crystals**

In order for donated holes or electrons to affect the conductivity of Si the Si must be in the form of a perfect, or nearly perfect crystal. Most metals or crystalline materials consist of a large number of micro-crystals. These are of the order of micrometers in size and the material is called polycrystalline. Si used for semiconductor device manufacturing is in a highly purified single-crystal form: The Si is melted and re-grown into a single large crystal.

## Equilibrium

Equilibrium of a Si crystal is a somewhat subtle concept. It means the crystal is not subjected to any net increase or decrease of energy and that the temperature is constant and doesn't vary throughout the crystal. In addition, the entropy of the system will be a maximum. Entropy is a measure of disorder in a system - it increases with increasing disorder. For example, the entropy of water in the form of ice is less than the entropy of the same amount of water when it is a liquid, since the atoms in a liquid are not as ordered as the atoms in an ice crystal. In statistical terms entropy can be expressed as  $S = -k \sum p_n \log(p_n)$ , where  $p_n$  is the probability the system will be in the  $n^{\text{th}}$  energy state. As the order increases and the number of states shrinks, the  $p_n$  vanish except for one of them, which approaches unity and  $S$  vanishes, that is, as the number of states shrinks,  $n \rightarrow 0$ ,  $n \ln(n) \rightarrow 0$ . As the number of states increases, increasing numbers of the  $p_n$  are non-zero, and  $S$  increases. From thermodynamics we have (First Law)  $dU = TdS - dW$  where  $U$  = energy,  $S$  = entropy and  $W$  is the work done (by the system). If the volume of the crystal is constant and the temperature is constant,  $dU = TdS$ . Since  $S$  = maximum,  $dS = 0$  and hence  $dU = 0$ . This is the condition of thermodynamic equilibrium.

## Mass action

This material involves more extensive use of thermodynamics than is usually covered in first year physics, but the material is not intrinsically more difficult than other 3<sup>rd</sup> year electrical engineering topics. It is somewhat lengthy but it should be understood in order to follow the arguments about recombination in this chapter.

The Law of Mass Action governs chemical reactions of the form  $2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O}$  or [electron-hole pair]  $\rightarrow$  [Si bond]. The notation used is as follows: when  $\nu_i$  molecules of initial reactant  $N_i$  produces  $\nu_j$  molecules of product  $N_j$ , we write  $\sum_i \nu_i N_i = 0$ . This means that the  $\nu_i$

are negative numbers since they represent reactants used up in the reaction. For example, in the production of water where  $2\text{H}_2\text{O} \leftrightarrow 2\text{H}_2 + \text{O}_2$  we write  $-2 \text{H}_2 - 1 \text{O}_2 \rightarrow 2 \text{H}_2\text{O}$  or

$-2 \times 2\text{H} - 1 \times 2\text{O} + 2 \times (2\text{H} + \text{O}) = 0$  or, without the symbols,

$-2 \times 2 - 1 \times 2 + 2 \times 3 = 0$ . For a reaction described this way, if the number of moles of the  $i^{\text{th}}$  constituent (reactant or product) is  $n_i$  and if  $\sum n_i = n$  where  $n$  is the total number of moles of material, then the concentration of the  $i^{\text{th}}$  constituent is  $n_i/n$ . The Law of Mass Action is then

$$\left(\frac{n_1}{n}\right)^{\nu_1} \left(\frac{n_2}{n}\right)^{\nu_2} \dots \left(\frac{n_i}{n}\right)^{\nu_i} \dots = \prod_i \left(\frac{n_i}{n}\right)^{\nu_i} = f(T) \quad (1)$$

where  $f(T)$  is a function of the temperature if the pressure of the system is constant.

In order to see how the Law of Mass Action comes about we confine ourselves to a system of ideal gases for which the Ideal Gas Law  $PV = nRT$  holds. For such a system the partial pressure of each gas is given by  $P_i = \frac{n_i}{n} P$  where  $P$  is the total pressure. The pressure can be

kept constant by allowing the reaction to take place in a vessel with one end a piston that exerts a constant force on the gas mixture. To proceed we need to review the First law of thermodynamics and the concept of entropy. We then define some new thermodynamic quantities designed for the specific problem at hand, called the Enthalpy and the Gibbs Function.

The First Law says that the change in energy  $U$  of a gas is equal to the heat added to the

gas less the work done by the expansion (change in volume) of the gas:

$$dU = dQ - dW \quad (2)$$

The heat  $dQ = TdS$ , where  $T$  is the temperature and  $S$  is the entropy. The work done by the gas is

$dW = PdV$ . Work done on the gas is  $dW = -PdV$ . Thus, if the volume decreases as work is done on the gas,  $dW < 0$ . The entropy  $dS$  is given by

$$dS \geq dQ/T \quad (3)$$

where the equality holds only for reversible processes. An example of a reversible process is one in which the volume of gas increases infinitesimally slowly as the gas does work on a piston. An irreversible process would be the rapid expansion of the gas volume with resulting turbulence set up in the gas. For a reversible process  $dU$  can be integrated exactly:  $dU$  is a perfect differential in the mathematical sense.

If we allow the possibility of a mixture of gases which can react chemically, to  $dU$  we must add a term  $\sum_i \mu_i dn_i$  which represents the energy extracted from or added to the system

when  $dn_i$  moles react, depending on whether the reaction is exothermic or endothermic, respectively.  $\mu$  is called the chemical potential: it represents the amount of energy absorbed or released per mole in a chemical reaction. Then

$$dU = TdS - PdV + \sum_i \mu_i dn_i \quad (4)$$

(for a reversible process). Since  $dU$  is a perfect differential for a reversible process we may write it in the form

$$dU = \left( \frac{\partial U}{\partial S} \right)_{V, n_i} dS + \left( \frac{\partial U}{\partial V} \right)_{S, n_i} dV + \sum_i \left( \frac{\partial U}{\partial n_i} \right)_{S, V} dn_i \quad (5)$$

where  $T = \left( \frac{\partial U}{\partial S} \right)_{V, n_i}$ ,  $P = - \left( \frac{\partial U}{\partial V} \right)_{S, n_i}$  and  $\mu_i = \left( \frac{\partial U}{\partial n_i} \right)_{S, V}$ . The subscripts on the

partials explicitly indicate the variables that are kept constant. The energy depends explicitly on  $S$ ,  $V$  and  $n$  (or several  $n_i$ ) - these are the natural variables for  $U$  and they are called extensive

variables; they depend on the amount of material in the system. If we write  $dU$  generally as  $dU \leq TdS - PdV + \sum_i \mu_i dn_i$  then we see that when a small change in  $S$ ,  $V$  or  $n$  doesn't

change  $U$ , that  $U$  must be a minimum. This is the equilibrium state of the system. For a system where the volume is allowed to change but the pressure is kept constant, the energy will no longer be a minimum in equilibrium and we must look for another function or potential to describe the system. The quantities  $P$ ,  $T$  and  $\mu$  are called intensive variables: they do not depend on the amount of material in the system ( $T$  doesn't double if the amount of material is doubled).

To find the new potentials we use a method developed by Euler. Suppose the extensive variables  $S$ ,  $V$  and  $n$  are increased by an amount  $\theta$  and the intensive variables are kept unchanged. Then  $U$  would change by the same factor  $\theta$ :

$$\theta dU = T\theta dS - P\theta dV + \mu\theta dn \quad (6)$$

(we consider just one species of gas in this example to simplify the notation). Put another way,

$$U(\theta S, \theta V, \theta n) = \theta U(S, V, n) \quad (6')$$

If this expression is differentiated with respect to  $\theta$  we find

$$\frac{d}{d\theta}(\theta U(S, V, n)) = U(S, V, n) = \frac{d}{d\theta} U(\theta S, \theta V, \theta n) = \frac{d}{d\theta} U(\theta X_j) \quad (7)$$

where  $X_1 = S$ ,  $X_2 = V$ ,  $X_3 = n$  etc. Then we have

$$U = \sum_j \frac{\partial U(\theta X_j)}{\partial(\theta X_j)} \frac{\partial(\theta X_j)}{\partial\theta} = \sum_j \frac{\partial U(\theta X_j)}{\partial(\theta X_j)} X_j = TS - PV + \mu n \quad (8)$$

When there is more than one species of gas the term  $\mu n$  is replaced by  $\sum_i \mu_i n_i$ . Before

proceeding we calculate the entropy and chemical potential of an ideal gas where  $dn = 0$ : the results will be needed shortly.

For an ideal mono-atomic gas at constant temperature

$$U = \frac{3}{2} nRT \quad (9)$$

From the first law we then have

$$dS = \frac{dU}{T} + \frac{P}{T}dV = \frac{\frac{3}{2} nRdT}{T} + \frac{nR}{V}dV \quad (10)$$

When this is integrated we get

$$S = nR \ln\left(\frac{T}{T_0}\right)^{\frac{3}{2}} + nR \ln\left(\frac{V}{V_0}\right) + S_0 \quad (11)$$

where  $S = S_0$  when  $T = T_0$  and  $V = V_0$ . If we now take into consideration the chemical potential of the gas and write the energy again as  $U = TS - PV + \mu n = 3/2 nRT$ , we can express the chemical potential as

$$\mu = -\frac{TS}{n} + \frac{PV}{n} + \frac{3}{2} RT = -T\frac{S}{n} + \frac{5}{2} RT \quad (12)$$

In terms of the entropy calculated above we obtain

$$\mu = -RT \ln\left(\frac{T}{T_0}\right)^{\frac{3}{2}} - RT \ln\left(\frac{V}{V_0}\right) - T\frac{S_0}{n} + RT \ln\left(e^{\frac{5}{2}}\right) \quad (13)$$

which can be simplified to

$$\mu = RT \ln\left\{\left(\frac{T_0}{T}\right)^{\frac{3}{2}} \left(\frac{V_0}{V}\right) e^{\frac{5}{2}}\right\} - T\frac{S_0}{n} \quad (14)$$

The quantity  $\frac{S_0}{n}$  is the entropy of 1 mole of gas at temperature  $T_0$  and volume  $V_0$ .

Note that if the volume of the gas is constant so no work is done by or on the gas,

$dU = dQ = 3/2 nRT$ . Then  $\frac{dQ}{dT} = \frac{3}{2}nR = C_v$ , which is the heat capacity of the gas at constant

volume.

Suppose now that instead of holding the volume of the gas constant we hold the pressure constant. We define a new potential  $H$  called the *enthalpy* as

$$H = U + PV \quad (15)$$

If we take the differential of H we get

$$dH = dU + PdV + VdP = TdS + VdP + \mu dn \quad (16)$$

The natural variables of H are those that appear as differentials: S, P and n.  $V = \left( \frac{\partial H}{\partial P} \right)_{S,n}$ .

If the pressure and number of moles of gas are constant so

$dP = dn = 0$ ,  $dH = TdS = dQ$  and  $\frac{dQ}{dT} = \frac{dH}{dT} = C_p$ , the heat capacity at constant pressure<sup>1</sup>.

Finally, we define the quantity

$$G = H - TS \quad (17)$$

called the Gibbs Function. G is very handy for calculations involving chemical reactions taking place at constant temperature and pressure. This is the case for reactions in a vessel in contact with a heat reservoir and sealed by a movable piston that applies a constant force. From

$$G = H - TS = U + PV - TS \quad (18)$$

we get

$$dG \leq TdS - PdV + \mu dn + PdV - VdP - TdS - SdT = \mu dn - VdP - SdT \quad (19)$$

If the temperature, pressure and number of moles of gas are constant, dG is negative or zero for an irreversible or reversible process, respectively, which implies G is a minimum.

We are now ready to see what happens when a chemical reaction defined by  $\sum_i \nu_i N_i = 0$  takes place. Recall that  $\nu_i$  is the number of *molecules* of substance  $N_i$  while  $n_i$  is the number of

<sup>1</sup> If P is constant, from  $dU = \frac{3}{2} nRdT = dQ - PdV$  we get, with

$$P = \text{constant} = \frac{nRT}{V}, \quad dQ = \frac{5}{2} nRdT. \quad \text{Thus } C_p = \frac{dQ}{dT} = \frac{5}{2} nR.$$

moles. From  $G = U + PV - TS$  and  $U = TS - PV + \sum \mu_i n_i$  we see

$$G = \sum \mu_i n_i \quad (20)$$

and

$$dG = \sum \mu_i dn_i \quad (21)$$

if T and P are constant.

We can now derive the Law of Mass Action for a mixture of ideal mono-atomic gases that undergo a chemical reaction. First we note that since ideal gases do not interact except to undergo a chemical reaction, their energies and entropies add. Suppose there are  $n_i$  moles of gas of type i (species  $N_i$ ) and that the total number of moles of gas is  $\sum_i n_i = n$ . The energy of species i is

$$U_i = \frac{n_i}{n_o} U_{oi} + \frac{3}{2} n_i R(T - T_o) \quad (22)$$

where  $U_{oi}$  is the energy of  $n_o$  moles of the gas that occupy a volume  $V_o$  when  $T = T_o$ . Similarly, the entropy of gas of species i is

$$S_i = \frac{n_i}{n_o} S_{oi} + \frac{3}{2} n_i R \ln \left( \frac{T}{T_o} \right) + n_i R \ln \left( \frac{V}{V_o} \times \frac{n_o}{n_i} \right) \quad (23)$$

$S_{oi}$  is the entropy of  $n_o$  moles of gas when  $T = T_o$  and  $V = V_o$ ; the factor  $\frac{n_o}{n_i}$  is due to the entropy

of mixing (it is, obviously, present only when more than one species of gas is present). The total energy and entropy are

$$U = \sum_i U_i = \sum_i n_i \left( \frac{U_{oi}}{n_o} \right) + \frac{3}{2} R(T - T_o) \sum_i n_i \quad (22')$$

and

$$S = \sum_i S_i = \sum_i n_i \left( \frac{S_{oi}}{n_o} \right) + \frac{3}{2} R \ln \left( \frac{T}{T_o} \right) \sum_i n_i + R \sum_i n_i \ln \left( \frac{V}{V_o} \times \frac{n_o}{n_i} \right) \quad (23')$$

The independent variables in the expressions are  $n_i$ ,  $T$  and  $V$ .

As a check on the validity of these expressions we can use them to derive the ideal gas law

$PV = nRT$ : from  $dU = TdS - PdV + \sum \mu_i dn_i$  we have  $\mathbf{P} = -\left(\frac{\partial U}{\partial V}\right)_{S, n_i}$ . By manipulating the

partial derivatives the pressure can be expressed as

$$\mathbf{P} = + \frac{(\partial S / \partial V)_{U, n_i}}{(\partial S / \partial U)_{V, n_i}} \quad (24)$$

This is done as follows: if  $U$  and the  $n_i$  are held constant,  $dU = 0$  and  $dn_i = 0$  for all  $i$ . Then

$dU = TdS - PdV + \sum \mu_i dn_i$  becomes  $0 = TdS - PdV$  or  $\mathbf{P} = T \left(\frac{\partial S}{\partial V}\right)_{U, n_i}$ . The temperature  $T$  is

given by  $T = \left(\frac{\partial U}{\partial S}\right)_{V, n_i}$  or  $\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{V, n_i}$ , and Equation 24 follows directly.

Similarly

$$\frac{1}{(\partial S / \partial U)_{V, n_i}} = \left(\frac{\partial U}{\partial S}\right)_{V, n_i} = \left(\frac{\partial U}{\partial T}\right)_{V, n_i} \left(\frac{\partial T}{\partial S}\right)_{V, n_i} \quad (25)$$

so we can write the pressure as

$$\mathbf{P} = \frac{(\partial S / \partial V)_{U, n_i}}{(\partial S / \partial U)_{V, n_i}} = \left(\frac{\partial S}{\partial V}\right)_{U, n_i} \left(\frac{\partial U}{\partial T}\right)_{V, n_i} \left(\frac{\partial T}{\partial S}\right)_{V, n_i} = \left(\frac{\partial U}{\partial T}\right)_{V, n_i} \frac{(\partial S / \partial V)_{U, n_i}}{(\partial S / \partial T)_{V, n_i}} \quad (26)$$

From the expressions for the energy and the entropy we can calculate:

$$\left(\frac{\partial U}{\partial T}\right)_{V, n_i} = \frac{3}{2} R \sum_i n_i \quad (27)$$

$$\left(\frac{\partial S}{\partial V}\right)_{U, n_i} = \left(\frac{\partial S}{\partial V}\right)_{T, n_i} = \frac{R}{V} \sum_i n_i \quad (28)$$

(using the fact that for the perfect gas if U is constant, T is constant) and

$$\left(\frac{\partial S}{\partial T}\right)_{V, n_i} = \frac{3}{2} \frac{R}{T} \sum_i n_i \quad (29)$$

From these partials we then get

$$P = \frac{3}{2} R \sum_i n_i \times \frac{\frac{R}{V} \sum_i n_i}{\frac{3}{2} \frac{R}{T} \sum_i n_i} = \frac{RT}{V} \sum_i n_i = \frac{nRT}{V} \quad (30)$$

so the ideal gas law has indeed been recovered. If P is multiplied by the concentration  $n_i/n$  of species i we find the partial pressure  $P_i = n_i \frac{RT}{V}$  of the  $i^{\text{th}}$  species.

Now assume that the mixture of gases undergoes a chemical reaction that produces new gas molecules, and that the temperature and pressure are maintained at constant values by using a heat reservoir and a constant pressure piston. Then with

$$G = \sum_i \mu_i n_i \quad (31)$$

we have

$$dG = \sum_i \mu_i dn_i \quad (32)$$

Let the number of moles be expressed in terms of the number of molecules by  $dn_i = \nu_i dx$  (this means  $dn$  is  $\frac{1}{\text{Avogadro's Number}}$  times a dimensionless differential  $dx$ ). If in the chemical

reaction  $\nu_i$  is a negative number this implies that  $n_i$  moles of gas i will be used up; if  $\nu_i$  is positive  $n_i$  moles will be created.  $dG = \left(\sum_i \mu_i \nu_i\right) dx$  and at equilibrium, when the reaction is over, G is a

minimum so  $dG = 0$ . This implies that

$$\sum_i \mu_i \nu_i = 0 \quad (33)$$

since a small change in  $dx$  must leave  $G$  unchanged (the meaning of a minimum). Now at constant volume the differential change in the energy  $U$  is

$$dU = TdS + \sum_i \mu_i dn_i \quad (34)$$

If we differentiate this expression with respect to  $n_k$  we get

$$\frac{\partial}{\partial n_k} \left( \sum_i \mu_i dn_i \right) = \frac{\partial}{\partial n_k} (dU - TdS) \quad (35)$$

Since  $\frac{dn_i}{dn_k} = \delta_{ik}$  where  $\delta_{ik}$  is the Kronecker delta (defined as  $\delta_{ik} = 0, i \neq k, \delta_{ik} = 1, i = k$ ), we

find the chemical potential

$$\mu_k = \left( \frac{\partial U}{\partial n_k} \right)_{V, T, n_i} - T \left( \frac{\partial S}{\partial n_k} \right)_{V, T, n_i}, \quad i \neq k \quad (36)$$

With

$$U = \sum_k n_k \left( \frac{U_{ok}}{n_o} \right) + \frac{3}{2} R(T - T_o) \sum_k n_k \quad (37)$$

the differentiation yields

$$\frac{\partial U}{\partial n_k} = \frac{U_{ok}}{n_o} + \frac{3}{2} R(T - T_o) \quad (38)$$

Now if we use Equation 23 for the entropy,

$$S = \sum_k n_k \left( \frac{S_{ok}}{n_o} \right) + \frac{3}{2} R \ln \left( \frac{T}{T_o} \right) \sum_k n_k + R \sum_k n_k \ln \left( \frac{V n_o}{V_o n_k} \right), \text{ differentiation gives us}$$

$$\frac{\partial S}{\partial n_k} = \frac{S_{ok}}{n_o} + \frac{3}{2} R \ln \left( \frac{T}{T_o} \right) + R \ln \left( \frac{V n_o}{V_o n_k} \right) - R \quad (39)$$

Putting all the terms together we get the chemical potential in terms of the initial energy and entropy, the temperature, the volume and the number of moles of the gases:

$$\mu_k = \frac{U_{ok}}{n_o} + \frac{5}{2} RT - \frac{3}{2} RT_o - \frac{TS_{ok}}{n_o} - \frac{3}{2} RT \ln \left( \frac{T}{T_o} \right) - RT \ln \left( \frac{V n_o}{V_o n_k} \right) \quad (40)$$

We can now manipulate this expression into a more useful form by using the Ideal Gas Law

$PV = nRT$  to write  $\frac{V_o}{n_o} = \frac{RT_o}{P_o}$  and  $\frac{V}{n_k} = \frac{RT}{P_k}$ . Then the product  $\frac{V n_o}{V_o n_k}$  becomes

$$\frac{V n_o}{V_o n_k} = \frac{RT}{P_k} \frac{P_o}{RT_o} = \frac{T P_o}{T_o P_k}. \quad \text{Finally, with a little algebraic manipulation the chemical}$$

potential of the  $k^{\text{th}}$  species is found to be

$$\mu_k = \frac{U_{ok} - \frac{3}{2} n_o RT}{n_o} + RT \left( \frac{5}{2} - \frac{S_{ok}}{R n_o} - \frac{5}{2} \ln \left( \frac{T}{T_o} \right) + \ln \left( \frac{P_k}{P_o} \right) \right) \quad (41)$$

or

$$\mu_k = F_k(T) + RT \ln \left( \frac{P_k}{P_o} \right) \quad (42)$$

where  $F_k(T)$  is a function only of the temperature. This is the key result, for if we now re-write the equation describing the chemical reaction

$$\sum_k \mu_k \nu_k = 0 \quad (33)$$

in terms of Equation 42 for  $\mu_k$  we obtain

$$\sum_{\mathbf{k}} v_{\mathbf{k}} \left( F_{\mathbf{k}} (T) + RT \ln \left( \frac{P_{\mathbf{k}}}{P_o} \right) \right) = 0 \quad (43)$$

or,

$$RT \sum_{\mathbf{k}} v_{\mathbf{k}} \ln \left( \frac{P_{\mathbf{k}}}{P_o} \right) = - \sum_{\mathbf{k}} v_{\mathbf{k}} F_{\mathbf{k}} (T) = A (T) \quad (44)$$

where A(T) is a function only of T. If we divide both sides of this expression by RT we have

$$\sum_{\mathbf{k}} \ln \left( \frac{P_{\mathbf{k}}}{P_o} \right)^{v_{\mathbf{k}}} = \ln \prod_{\mathbf{k}} \left( \frac{P_{\mathbf{k}}}{P_o} \right)^{v_{\mathbf{k}}} = - \frac{A (T)}{RT} \quad (45)$$

or, using the relation between the partial pressures of the gases,  $\frac{P_{\mathbf{k}}}{P} = \frac{n_{\mathbf{k}}}{n_o}$

$$\sum_{\mathbf{k}} \ln \left( \frac{n_{\mathbf{k}} P}{n_o P_o} \right)^{v_{\mathbf{k}}} = \ln \prod_{\mathbf{k}} \left( \frac{n_{\mathbf{k}} P}{n_o P_o} \right)^{v_{\mathbf{k}}} = - \frac{A (T)}{RT} \quad (45')$$

or

$$\ln \prod_{\mathbf{k}} \left( \frac{n_{\mathbf{k}} P}{n_o P_o} \right)^{v_{\mathbf{k}}} = - \frac{A (T)}{RT} \quad (45'')$$

By taking the anti-logarithm of both sides of this last equation we get the Law of Mass Action:

$$\prod_{\mathbf{k}} \left( \frac{n_{\mathbf{k}}}{n_o} \right)^{v_{\mathbf{k}}} = \left( \frac{P}{P_{\mathbf{k}}} \right)^{\sum_{\mathbf{k}} v_{\mathbf{k}}} e^{-\frac{A(T)}{RT}} = \left( \frac{P}{P_{\mathbf{k}}} \right)^{\sum_{\mathbf{k}} v_{\mathbf{k}}} K(T) = f (T) \quad (46)$$

where f(T) is a function only of the temperature if P is constant. That is, the product of the concentrations  $n_{\mathbf{k}}/n_o$  raised to the power  $v_{\mathbf{k}}$  is a function only of the temperature if the pressure P is constant.

## Mobility

Here is a simplified argument for the equation  $\mu = \frac{q\tau}{m}$ . Recall that the mobility  $\mu$  is defined

by  $\bar{v} = \mu E$  where  $\bar{v}$  is the average, or drift speed and  $E$  is the electric field strength. Suppose the average distance an electron or hole travels between collisions is  $l$  and the average time between collisions is  $\tau$ ; when there is a collision the particle changes direction and begins to accelerate in the direction of the electric field again. The average speed is then  $\bar{v} = \frac{l}{\tau}$  and the

average momentum is  $\mathbf{p} = m\bar{\mathbf{v}}$ . The particle is subject to a force  $F = qE$  due to the electric field.

From  $\mathbf{F} = \frac{d\mathbf{p}}{dt}$  we can identify the force  $F$  with the momentum divided by the time between

collisions, or, conversely,  $\mathbf{p} = m\bar{\mathbf{v}} = \mathbf{F}\tau = qE\tau$ . We then have:  $\bar{v} = \mu E = \frac{p}{m} = \frac{qE\tau}{m}$  or,

cancelling the common factor  $E$ ,  $\mu = \frac{q\tau}{m}$ . A tighter argument can be made by calculating the

average speed and mean free path using appropriate distribution functions, but the result is the same.

## Drift velocity

We see that the drift velocity of an electron in a field of  $1 \text{ V cm}^{-1}$  is not particularly high and is equal to the velocity an electron would attain in free space in a few nanoseconds. The reason for this is that the electrons have frequent elastic collisions in which they change direction and hence velocity. Free electrons in Si have an average kinetic energy determined by the temperature. At room temperature this is about  $0.025 \text{ eV}$ , which corresponds to a velocity of

$$v = \sqrt{\frac{2q \times 0.025}{m}} = 6.7 \times 10^6 \text{ cm sec}^{-1}. \text{ An electric field of about } 5 \times 10^3 \text{ V cm}^{-1} \text{ gives a}$$

drift velocity of this size. It is found experimentally that the drift velocity becomes independent of the electric field when it is about twice the thermal velocity - the velocity "saturates". The reason is that collisions happen so frequently that the electron can't gain any more speed no matter how strong the field.

## Current density

Current density is related to the concept of flux. This concept is easily understood using familiar terms. Suppose there are people exactly five feet high passing through a doorway ten feet wide and five feet high. If the people take up one square foot each, their density is one person per five cubic feet. If they move through the doorway at a speed of one foot per second, then ten people will move through the ten foot wide doorway per second. The density of the people multiplied by their velocity is  $\rho v = 1/5 \text{ ft}^{-3} \times 1 \text{ ft sec}^{-1} = 1/5 \text{ ft}^{-2} \text{ sec}^{-1}$ . The flux  $F$  of people is defined as the number per second per square foot. In this case the number of people is ten per second divided by the area  $A$  of the doorway, which is  $A = 5 \times 10 = 50 \text{ ft}^2$ . Therefore we find  $F = 10 \text{ sec}^{-1} \div 50 \text{ ft}^2 = 1/5 \text{ ft}^{-2} \text{ sec}^{-1} = \rho v$ . In the case of electric current we multiply the number density of the holes or electrons,  $p_o$  or  $n_o$  ( $\text{cm}^{-3}$ ), respectively, by the charge  $\pm q$  to get the current density  $J$  ( $\text{C cm}^{-2} \text{ sec}^{-1} = \text{A cm}^{-2}$ ).

## Resistivity of Si

To get a feel for the resistivity of Si, consider three cases: (1) intrinsic Si ( $n_o = p_o = n_i$ ); (2) n-type Si with  $N_d = 1 \times 10^{18}$ ; and (3) p-type Si with  $N_a = 1 \times 10^{17}$ . In the first case

$$\begin{aligned}\sigma &= q(n_o\mu_e + p_o\mu_h) \\ &= 1.6 \times 10^{-19} \text{ C} \times 1 \times 10^{10} \text{ cm}^{-3} \times (1500 + 600) \text{ cm}^2 \text{ V}^{-1} \text{ sec}^{-1} \\ &= 3.36 \times 10^{-6} (\Omega\text{-cm})^{-1}\end{aligned}$$

Therefore the resistivity is  $\rho = 1/\sigma = 3 \times 10^5 \Omega\text{-cm}$ . In the second case  $n_o = 1 \times 10^{18}$  so  $p_o = 100$ , which is completely negligible.  $\sigma = 1.6 \times 10^{-19} \times 1 \times 10^{18} \times 1500 = 240 (\Omega\text{-cm})^{-1}$  so  $\rho = 4.2 \times 10^{-3} \Omega\text{-cm}$ . Finally, in the third case  $p_o = 1 \times 10^{17}$  so  $n_o = 1000$ , which is again negligible. Then  $\sigma = 9.6 (\Omega\text{-cm})^{-1}$  and  $\rho = 0.1 \Omega\text{-cm}$ .

## Diffusion

The mathematics of diffusion can get involved, but if we limit ourselves to one-dimension it's pretty straightforward. This is not much of a limitation because when we consider diffusion in a semiconductor device the one-dimensional approximation is good.

The simplest conceptual picture of diffusion is probably the motion of ink molecules in water. Imagine a small drop of ink placed carefully into a glass of still water (a glass of water at uniform temperature that has been sitting untouched for a few days, so there are no currents in it). From experience we know that the ink drop will slowly spread out and that, if we wait a long time, the ink molecules will eventually be distributed uniformly throughout the glass. What is happening is that the molecules are moving from regions of high ink density to regions of low ink density. Why do they do this? Here is a simple analogy. Imagine a basketball court aligned along a north-south line with the north half having one person every square foot and the south half having one person every ten square feet. If the people move randomly but only towards one basket or the other, then at any given time half the people will be moving towards the south basket and half towards the north basket. Near the center court there will be, on the average, ten times as many people moving south as moving north and so, after a while the densities of people will start to equilibrate.

Now consider the following situation: particles are arranged in three dimensions but can move only along the direction of the x-axis. The particles have an average speed  $v_x$  and their density  $\rho$  is a function of x:  $\rho = \rho(x)$ . Consider a plane perpendicular to the x-axis at location x and another plane perpendicular to the x-axis but located at  $x + dx$ . The density of particles at the first plane is  $\rho(x)$  and the density at the second plane is  $\rho(x+dx)$ . The average number of particles  $\text{cm}^{-2} \text{sec}^{-1}$  moving from the plane at x towards the plane at  $x + dx$  will be  $\frac{1}{2} \rho(x) v_x$  and the average number of particles  $\text{cm}^{-2} \text{sec}^{-1}$  moving towards the plane at x from the plane at  $x + dx$  will be  $\frac{1}{2} \rho(x+dx) v_x$ . The net number of particles per  $\text{cm}^2 \text{sec}^{-1}$  crossing the plane at x will then

be  $-\frac{1}{2} v_x (\rho(x+dx) - \rho(x)) = -\frac{1}{2} v_x \frac{d\rho}{dx} dx$  so the flux F of particles is proportional to the

derivative of the density:  $F = -\text{constant} \cdot \frac{d\rho}{dx}$ . The constant has units of  $\text{cm}^2 \text{sec}^{-1}$  and is called

the diffusion constant. The minus sign means the flow is *away* from the high density region.

## Non-linear equation

Although non-linear differential equations are in general very difficult to solve, there is one almost obvious case where the solution is easy: if the generation rate  $g(t)$  is very large and then shuts off, and if  $n \gg n_0 + p_0$ , the equation becomes  $\frac{dn}{dt} \approx -K(T) n^2$  or, with

$$K(T) = \frac{1}{(n_0 + p_0)\tau_0}, \quad \frac{dn}{dt} \approx -\frac{n^2}{(n_0 + p_0)\tau_0}. \quad \text{This is easily integrated to give}$$

$$\frac{1}{n(t)} - \frac{1}{n(0)} = \frac{t}{(n_0 + p_0)\tau_0}, \quad \text{or, re-arranging, } n(t) = \frac{n(0)(n_0 + p_0)\tau_0}{n(0)t + (n_0 + p_0)\tau_0} \text{ which, for}$$

large values of  $t$ , decreases linearly with  $t$ .

## Equation of continuity

The easiest way to understand the equation of continuity is to consider a gas, which consists of a very large number of particles  $\text{cm}^{-3}$ , so that we can define a density. Now, take some small volume of gas in a volume  $dV = A dx$ , where  $A$  is the area of a side of the volume perpendicular to the  $x$ -axis. The mass of material in the volume is the  $\rho dV = \rho A dx$ . Let the flux of gas molecules into the volume at  $x$  be  $J(x)$  and the flow out of the volume at  $x + dx$  be  $J(x + dx)$  ( $J$  has units of  $\text{gm cm}^{-2} \text{sec}^{-1}$ ). Then the time rate of change of the mass due to the net flow out of the volume will be  $[J(x) - J(x + dx)] A = - \frac{\partial J(x)}{\partial x} dx A$ . The rate of change of the

mass of gas in the volume due to the change in density is  $\frac{\partial \rho}{\partial t} dV = \frac{\partial \rho}{\partial t} dx A$ . The total rate

of change of the mass of gas must be zero since matter is conserved, so

$$\frac{\partial \rho}{\partial t} dx A = - \frac{\partial J}{\partial x} dx A \quad \text{or} \quad \frac{\partial \rho}{\partial t} + \frac{\partial J}{\partial x} = 0.$$

## Relaxation time

Suppose you were to place a quantity of electric charge  $Q$  in doped Si. The charge is initially contained in a small volume  $v_0$  of radius  $a$ . The Si has dielectric constant  $\epsilon$  and conductivity  $\sigma$ . Since like charges repel the charge would spread itself out as much as possible and, after some time, most of it would have left the initial volume. How long would it take for the amount of charge in  $v_0$  to be reduced by  $1/e$ ? This time can be found by using the equation of continuity  $\frac{d\rho}{dt} + \nabla \cdot \mathbf{J} = 0$  and  $\mathbf{J} = \sigma \mathbf{E}$ . Since  $\nabla \cdot \mathbf{E} = \frac{\rho}{\epsilon}$  we immediately have  $\frac{d\rho}{dt} + \frac{\sigma}{\epsilon} \rho = 0$

which, when integrated, gives us  $\rho = \rho_0 \exp^{-\frac{\sigma}{\epsilon} t} = \rho_0 \exp^{-\frac{t}{\tau_\epsilon}}$  where  $\tau_\epsilon = \frac{\epsilon}{\sigma}$  is the dielectric

time constant. For n-type Si with doping  $N_d = 10^{17}$ ,  $\sigma = qn_0\mu_e = 24 (\Omega\text{-cm})^{-1}$  while the dielectric constant of Si is  $11.8 \epsilon_0 \approx 10^{-11} \text{ F cm}^{-1}$ , so  $\frac{\epsilon}{\sigma} \approx 4 \times 10^{-13} \text{ sec}^{-1}$ . Thus the relaxation

time is very short.

## Density distribution

An example: finding the density distribution of holes in n-type Si when there is a source of electron-hole pairs given by  $g(x) = \text{constant} = G$  over part of the length of the Si. Assume the Si is doped with donors at a density  $N_d$  and that the Si has a length  $W$ . Assume also that  $g(x) = 0$  for  $x \leq W_1$  and for  $x \geq W_2$  and that there are metallic contacts at  $x = 0$  and  $x = W$  so that  $p(0) = p(W) = 0$ .

For  $x \leq W_1$  and for  $x \geq W_2$  the equation for the holes is  $\frac{d^2 p}{dx^2} - \frac{p}{L_h^2} = 0$ , with boundary

conditions  $p(0) = p(W) = 0$ . For  $W_1 < x < W_2$  we have  $\frac{d^2 p}{dx^2} - \frac{p}{L_h^2} = -\frac{G}{D_h}$ . A condition we

can impose on the carrier densities is that they and their first derivatives be continuous functions of position, because if they were not that would imply discontinuities in the current density, which would be unphysical.

In the regions where  $g = 0$  the solutions are  $A e^{x/L_h} + B e^{-x/L_h}$  for  $x \leq W_1$  and  $C e^{x/L_h} + D e^{-x/L_h}$  for  $x \geq W_2$ . At  $x = 0$  we have  $B = -A$  so that  $p(x) = 2A \sinh(x/L_h)$ . At  $x = W$  we have  $D = -C \exp^{-2W/L_h}$  and so  $p(x) = C \exp^{W/L_h} \sinh\left(\frac{x - W}{L_h}\right)$ .

Where  $g(x) = G$  we have a non-homogeneous differential equation. The homogeneous part is the same as before and so the solution is again  $E \sinh(x/L_h)$ . To these we add a particular solution equal to a constant, so  $p(x) = E \sinh(x/L_h) + \text{const}$ . When this is put into the differential

equation we get  $\frac{E}{L_h^2} \sinh\left(\frac{x}{L_h}\right) - \frac{1}{L_h^2} \left( \sinh\left(\frac{x}{L_h}\right) + \text{const} \right) = -\frac{G}{D_h}$

so the value of the constant is  $\text{const} = \frac{GL_h^2}{D_h}$ . We then require that  $p(x)$  and  $\frac{dp}{dx}$  be continuous

at  $x = W1$  and at  $x = W2$ , which gives the values for A, C and E in terms of W1 and W2. Once these constants are known the current densities can be found for all values of x, as well as the electric field in the Si.

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