

Practically, all materials acquire a charge when touched or made contact by a dissimilar material. This contact-charging phenomenon can be the result of the combination of any metal (conductor), semiconductor, or dielectric (insulator), which are brought into contact. It is particularly important that the following discussion of the phenomena of contact electrification will begin with a discussion of metal-metal contacts. This is because the theory of the contact electrification of metals has been successfully described with no existing conflict of ideas, and used primarily as a basis for many attempts to explain the contact charging mechanisms of other combinations: i.e., metal-insulator and insulator-insulator.

a) Metal-Metal Contacts

In looking over the theory of the contact electrification, undoubtedly, contact charging of metals is of great significance. It is often thought that the charge transfer between two metals by contact electrification is rather improbable, since the charging of metals is not quite noticeable under most circumstances. Indeed, the charge transfer across the interface between two metals, when the two metals with difference in work functions are brought into contact, may be greater than the charge transfer between a metal and an insulator. However, the high conductivity of the metals allows the charge to run away readily from the region of contact. Moreover, the charge back-flow that usually occurs as the materials are parted happens very quickly in the case of poor insulator (or metal), so that the total charge deposited remains relatively small. Nonetheless, the contact electrification of metals should be carried out in a vicinity where there is no electric field or stray alternating fields, because such fields can cause charge transfer by any means but normal contact (for instance, induction).

The mechanism of charge transfer in metals is quite crystal-clear, considering the electron states in metals are reasonably simple and well understood. In metals, there is a band of allowed electron states that is filled up to the Fermi energy, E_F . The work function, ϕ , of the metal is the amount of energy by which its Fermi level lies below the vacuum level. When two metals with different work functions, ϕ_A and ϕ_B , are in contact, the charge transfer occurs in such a way that the electrons flow from the metal with the higher Fermi energy in to that with the lower Fermi energy (figure 1.3). The transfer of these

electrons increases the electron potential of B relative to A and terminates when the Fermi energies of A and B equalize. Accordingly, the charge transfer should be proportional to the difference in the work functions between the two metals,

$$Q \propto (\mathbf{f}_B - \mathbf{f}_A). \quad [1.3.1]$$

Apparently, the theory of the contact electrification of metals is based on the assumption that; when two metals are in contact with each other, charge is transferred between them until their Fermi levels are brought into coincidence. The electrons are exchanged between those two metals so that they come into *thermodynamic equilibrium*; that is the electrochemical potentials are the same throughout the two metals. Then the difference in the surface potentials of metals will be

$$V_c = (\mathbf{f}_B - \mathbf{f}_A) / e, \quad [1.3.2]$$

Where V_c is called the *contact potential difference*. It seems, therefore, that the charge on the metals during their contacts is given by the aftermath of V_c and the effective capacitance between them.

The situation when the metals are separated after contact is also of importance in the theory of contact electrification of metals. Harper (1967) pointed out that electrons will tunnel between the metals while they are separating, as long as the distance between them is small enough. As the metals separate, the capacitance between the two metals is found decreasing and the surface potential difference for a given charge becomes increasing. In trying to retain the thermodynamic equilibrium, electrons will tend to tunnel across the gap between the metals, so that the potential difference is maintained equivalently to V_c . Ultimately, the charge on the metals after separation should approximately be

$$Q = C_0 V_c, \quad [1.3.3]$$

where C_0 is the contact capacitance between the bodies at the critical separation z_0 , defined as the point whereat the resistance between the two bodies increases very sharply while the capacitance changes

relatively slow. According to Harper, C_0 is a constant that depends only on the shape of the contacting bodies and is normally determined by the degree of roughness of the contacting surfaces.

It has been experimentally confirmed by many researchers (Lowell and Rose-Innes, 1980) that the charge transfer between two metals is proportional to their contact potential difference (Figure 1.4). This also includes the finding that the contact charge does not depend on the speed of separation. In summary, the electron back-flow by tunnelling has been found not to cause the decrease of the charge on the metals after separation. It may be said that the charge on the metals is entirely determined by the coincidence of the Fermi energies of the two metals on contact, or by the thermodynamic equilibrium.

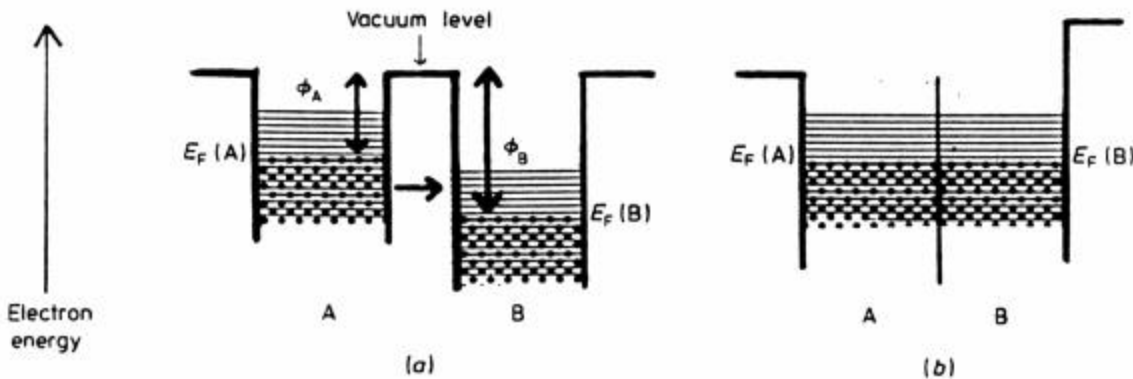


Figure 1.3. Two metals, A and B: (a) before contact, (b) after contact. (after Lowell and Rose-Innes (1980))

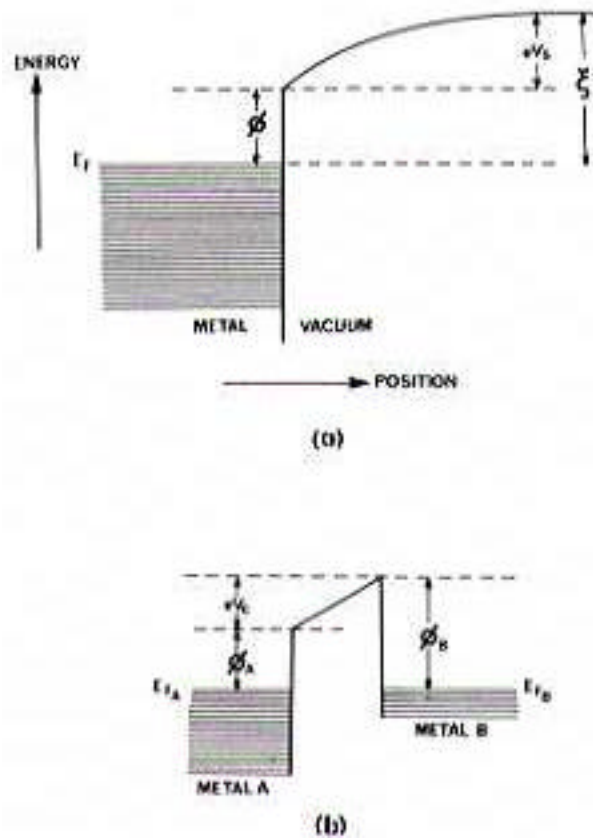


Figure 1.4. The variation of the energy of an electron inside and outside a metal is shown in (a). V_s is the surface potential and ϕ is the work function. E_F is the minimum energy of an electron added to the metal. Two metals in close proximity (b) exchange charge until, in equilibrium, their Fermi levels are coincident. The transferred charge is such as to cause a difference in surface potential equal to $(\phi_B - \phi_A) / e$, that is, the contact potential difference V_c . (after Lowell and Rose-Innes, 1980)

b) Metal-Insulator Contacts

Contact electrification is oftentimes confined to insulators, owing especially to their abilities of accumulating charge in ways that the metals cannot; therefore, the charge on the insulators is usually very observable. The term ‘insulator’ normally covers a very wide range of materials varying in structure, with only one common feature of being poor conductors of electricity. Work on the contact electrification of insulators is often performed by contacting the insulators with metals since the behavior of a metal in contact electrification has been well understood. In that case, the results can be smoothly interpreted. Still, the contact electrification between insulator and metal does require a good knowledge of the electron states in insulators, which at present falls far short of understanding, specifically at their surface. It is noted that: when an insulator is in contact with a metal, the charge acquired by the insulator may depend not only on the nature of insulator itself, but also, in some cases, on the specific metal and on the type and duration of contact.

It has been quantitatively established for a long time that the charge transferred between an insulator and a metal tends to correlate with the difference in work function between the two materials. This correlation suggests that, for the contact electrification of metal and insulator, the charge transfer be by electrons rather than by ions or else. Note that the charge transfer by ions or material has yet been completely excluded. It has also been assumed that the charge is transferred between the metal and the insulator until thermodynamic equilibrium is established. This assumption is based on the same theory as which applicable to metals. It is described that each insulator is supposed to have ‘Fermi level’, E_0 , which, after contact, becomes coincidence with the Fermi level of the metal. After a large number of investigations, it is now recognized that the charging of solids involving the insulators should occur primarily at the surface, and that there are sufficient electron sites in the insulators to account for the charge. Moreover, it has been suggested that the thermodynamic equilibrium model may not be valid for insulators with a wide energy gap. An alternative mechanism for charge transfer has then been proposed, indicating that the tunnelling of electrons between the metal and localized states in the insulator may play an important role in the charge transfer. The detailed mechanism will be discussed in the following section.

ii) Mechanisms of Charge Transfer

According to Harper (1967), the three primary ways in which charge can transfer from one substance to another are i) by electron transfer, ii) ion transfer, and iii) material transfer. There is important evidence suggesting that, in triboelectrification of coal and mineral matters, the charge transfer be often due to electrons. Nonetheless, the other two charging mechanisms may occur in some particular cases, and they are worthwhile to be remarked here, in brief.

a) Material Transfer

There is compelling evidence that the contact of two solids can result in the transfer of material from one to another. Material transfer in some cases (such as, when polymers and metals are brought into contact) is of possible notability to contact electrification, if the number of transferred atoms per unit area exceeds the charge density (in units of e per unit area) observed in the contact electrification (Lowell and Rose-Innes, 1980). As a result of material transfer, charge transfer will occur if the transferred material carries charge. The fact that the conditions at the surface of a material are basically not the same in the interior indicates that the surface of the material may carry a layer of charge. Metals and semiconductors are good examples of such a circumstance. Metals are ordinarily coated with their oxides that usually carry the net charge compensated by charge in the underlying metals. For a semiconductor, charge may reside in its surface states and be compensated by charge of the opposite sign distributed in the interior.

Probably the most convincing evidence of mass transfer is the work of Salanek and his group (Salanek et.al., 1976). With the use of ESCA for surface analysis, they showed that some of the metal transferred to the polymer and, likewise, some of the polymer to metal when they were in contact with each other. Moreover, very large amounts of polymer may transfer to the metal during the time that the metal slides over polymer (Pooley and Tabor, 1972). But in spite of what has been reported, those

cases where material transfer has been shown taking place were analytically found not to be the first primary cause of charge transfer. As addressed in the work of Salanek et.al., the large amounts of material transferred were observed in the first contact between a metal and polymer, but the significant increase in the amount of material transferred did not happen for the second and following contacts.

Furthermore, there is the other supporting evidence that material transfer is unlikely to be a primary cause of the contact electrification of metal-insulator. A paper published by Lowell (1977) reported that the same region of polymer surface may be repeatedly charged to approximately the same extent by repeated contacts with a metal. Note that the charge on the surface should be removed between contacts for such case. It is also important to bear in mind that, if a metal charges a polymer because of material transfer, one would expect charge transfer to be practicable only if the two materials have not previously in contact.

b) Ions Transfer

Contact electrification has been suggested by a number of researchers (Shaw, 1917; Henry, 1957; Harper, 1967; Kornfeld, 1976; Ruckdeschel and Hunter, 1977) that the charge transfer occurred may be due to the transferring of ions from one surface to the other. However, it is difficult to accept this suggestion as the mechanism of charge transfer usually occurred in the case of metal-insulator contacts, although some researchers were influenced to believe so. Only in the case of insulator-insulator contacts, there is a great deal of experimental evidence that ion transfer may be a dominant mechanism for the charge transfer. Or even two or three mechanisms (electron, ion and material transfer) may contribute simultaneously to the charge transfer in some particular cases.

Evidently, the most far-reaching affirmation for the ion transfer model has been made by Kornfeld (1974). He claimed that the circumstances in which the surfaces of the same materials may charge each other, and that the sign of the charge transferred to one surface when it is rubbed by another may eventually change as rubbing continues, can be explained by the ion transfer mechanism. He pointed out that insulators, in general, carry a net internal charge because of charged defects in the

crystal lattice; this internal charge is neutralized by ions on the surface. These ions are attracted to the surface from the atmosphere, which is always slightly ionized. It is also suggested that different surfaces have different affinities for a given ion, hence, there will ordinarily be a transfer of ions from one surface to the other when two ion-coated surfaces are brought into contact. Nevertheless, Kornfeld's ion-transfer mechanism has been disputed by the more convincing and nearly overwhelming evidence shown by other workers. Those results controversially indicated that electron transfer should be the dominant mechanism when metal is one of the contacting materials. Moreover, Lowell and Rose-Innes (1980) pointed out that charge transfer between insulators is also attributed to electrons. They included that the electrification of one insulator by another can be predicted from the information on the triboelectrification of each of insulators by metals.

Harper (1967) has several papers contributing to the study of ion transfer mechanism. He found very large charge transfer on quartz and concluded that the charge transfer should be credited to a thick layer of -OH ions which were present on the quartz surface as a result of the manner in which it was prepared. Contrary to what has been reported by Harper, a work performed on quartz by Wagner (1956) indicated electron transfer as the charging mechanism when charging quartz against metals. His indication was attributed to the finding of the relationship between the charging and the work function of the contacting material. Yet, the ion transfer was not completely denied to be a possible mechanism for the electrification of some substances, such as Al_2O_3 , MgO , and the alkali halides. Furthermore, a number of studies in connection with the ionic mechanisms of charge transfer were carried out on pyroelectric insulators (Harper, 1967; Kornfeld, 1974; Robins et.al, 1975). It appears eventually that the contact electrification is influenced by the polarization of the pyroelectric material, but not by the presence of compensating ions.

The ion transfer mechanism when water is present on surface is also of particular interest, in addition to the transfers of ions attached to dry surfaces that have been discussed above. There is compelling evidence that contact charging of insulators may be varied by the presence of water. Harper (1967) has proposed that charge transfer might appear through a kind of *electrolytic process*. Such electrolytic charging is regarded as a process in which ion moves in a superficial water layer. An

extensive series of experiments, which suggest the electrolytic charging, has been described by several authors since early century. Knoblauch (1902) found a strong correlation between the sign of charging and acidic or basic properties (the presence of H^+ and OH^-). Moreover, he proposed a mechanism to explain the charging of some totally insoluble materials, and concluded that the charging occurred as a result of the attraction of H^+ or OH^- ions present in a (probably contaminated) water layer to the material of greater dielectric constant. His findings were confirmed by Rudge (1914), who was unaware of the similar works he had carried when compared with those of Knoblauch. Years later, Medley (1953) conducted his experiments on polar polymers. His work became more evident to electrolytic charging, with the result denoting that the polar polymers would acquire electrical conductivity in a humid atmosphere due to electrolytic dissociation in absorbed water. In summary, water may influence contact electrification in an indirect way, by increasing the conductivity of the insulator.

Turning now to the concept of ion transfer which may be considered in the case of insulator-insulator contacts rather than in the contact electrification of metal-insulator. Up to present, no comprehensive theory of ion transfer has been developed yet. But the redistribution of positive and negative ions between two surfaces, which have just been in contact, has been intensely contemplated by Henry (1957). Henry proposed an indicative theory in which the several different driving forces, which could transfer ions from the surface of one insulator to another, were pulled into observance. An expression was derived for the charge transfer involving all these effects. To make it rather more explicit, Lowell and Rose-Innes (1980) considered treating them separately, and their treatment should thus be followed.

As shown in Figure 1.5, the potential energy of an ion is given as a function of its position between two nearly separated parallel surfaces, and the vibrational levels are indicated. This potential includes that as a result of excess charge on the insulator surfaces. Basically, ions will concentrate near the minima adjacent to the two surfaces when in equilibrium. The number n_1 and n_2 of ions close to surface 1 and 2, respectively, will be assigned approximately by

$$n_1 / n_2 \sim \exp (- \Delta U / kT), \quad [1.3.4]$$

where ΔU is equal to $U_1 - U_2$ (Figure 1.5). ΔU is defined as an energy difference between the lowest vibrational levels in the two troughs at cut-off; simply put, it is the energy difference between the minima shown in the figure. The equilibrium may not be reached for a very long time if U_1 and U_2 are large compared to kT , but it will be disregarded at the moment. Furthermore, it is presumably for the time being that ions in the two minima remain attached to their individual surfaces after separation.

If ΔU is considerably larger than kT , equation (1.3.4) will thus suggest that most of the ions would collect on one of the surfaces. However, if there are a lot of ions, ΔU will be modified by the electric field formed when those ions transfer. Obviously, all the ions will transfer to one surface if the total charge is less than σ_0 , where

$$(e\sigma_0 / \epsilon_0) z \approx \Delta U . \quad [1.3.5]$$

It is assumed that the distance between the minima in Figure 1.5 is the order of the separation z of the surfaces. Correspondingly, if the ions on the two surfaces have total charge larger than σ_0 , the charge transfer will proceed until the field is adequate to make the energies of the two minima equal. If ΔU is the initial energy difference between the minima, the charge transferred is given by

$$(e\sigma z / \epsilon_0) = \Delta U . \quad [1.3.6]$$

It is difficult to predict the charge density numerically with no information of ΔU or of the effective separation, z . However, a rough computation can be done by assuming z to be so small that ΔU is less than ~ 1 eV, so the thermionic emission of one surface to another while the two are in contact will not be very slow. It is noted that ΔU would be ≥ 1 eV in general if the binding energies of the ions to the surface are bigger than 1 eV, except that the surfaces are closer than ~ 0.3 nm so that the image forces reduce ΔU . Therefore, it is essential that z must be assumed ≤ 0.3 nm for contact electrification to happen. By substituting these numbers in equation (1.3.6), one can find $\sigma = 3 \times 10^{-2}$

C/m^2 as the condition for equation (1.3.5) to be satisfied. But the observed charge densities are nearly always smaller than this and equation (1.3.6) is, therefore, usually irrelevant.

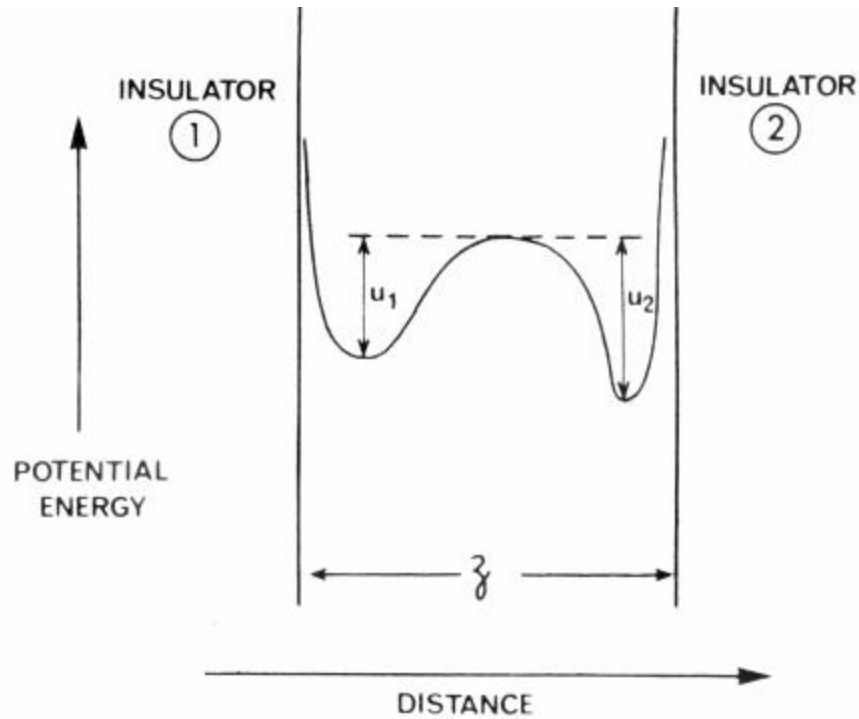


Figure 1.5. Dependence of the potential energy of an ion on its position between two plane parallel insulator surfaces (Lowell and Rose-Innes, 1980).

If the binding energy of a given ion is supposedly different on dissimilar insulator surfaces, by the amount ~ 1 eV or more, the above mechanism will always be the dominant one. But once the two insulators are identical, the binding energy will spontaneously not differ, and make the small effects become important. There is evidence that these effects may cause the charge transfer between the identical insulators. Henry is of the opinion that there are two ways in which the identical insulators may charge each other. The first is what he calls the “abundance effect”. If the densities of ions on the two surfaces were, by chance, unequal, some charge would transfer from one to another during contact. Nevertheless, this effect is obviously not the mechanism that occurs on a regular basis.

The second, the “temperature effect” is a particularly important effect of the ionic transfer mechanism. It is well noticed that charge transfer between two identical insulators can occur as a result of a temperature difference, especially when these identical insulators are rubbed together. It is pointed out that a degree of asymmetry is often introduced when two objects are rubbed together, and this applies also to the rubbing of the two identical bodies (Harper, 1967). It may be that this asymmetry generates a temperature difference between the contacting surfaces, causing the charge transfer.

If there is a temperature difference, the system is not in thermodynamic equilibrium and equation (1.3.4) is not valid. Therefore, the pre-exponential terms are ignored and one can see that for dynamic equilibrium

$$(U_1 / T_1) \approx (U_2 / T_2), \quad \text{or} \quad \Delta U \approx (\Delta T / T_1) U_1, \quad [1.3.7]$$

where ΔT is the temperature difference, $\Delta T = T_2 - T_1$, and $\Delta U = U_2 - U_1$. Eventually, for identical surfaces, one can find that

$$\sigma = (\epsilon_0 U_1 / zeT_1) \Delta T. \quad [1.3.8]$$