

## Chapter 2. Gas Phase Collision Processes

In the last chapter we considered the behaviour, both microscopically and macroscopically, of gases. Although that consideration was primarily of neutral ground state molecules, we shall see later that some of the concepts are useful in dealing with charged particles also.

Although the glow discharge is an integral part of each of the several processes that we're dealing with, the discharge is performing only a functional role in each case. We are able to group these processes together because the type of discharge is reasonably common: the degree of ionization is typically  $10^{-4}$ , and the current densities are of the order of  $1 \text{ mA/cm}^2$ , so that essentially we still have a neutral ground state gas that can be described by the gas laws. The prime feature of these discharges is that of ionization, with perhaps as many as  $10^{18}$  electron-ion pairs being produced per second. But the different processes make use of ionization in different ways. For example, in the physical process of sputtering, the main requirement is an adequate supply of ions that can be accelerated onto a target to produce sputtering. In plasma etching, a principal requirement is a process to dissociate relatively stable gas molecules into chemically active species which can then react with the substrate; this dissociation is efficiently carried out by electron impact, and in turn these electrons rely on the ionization process for their sustenance. Inevitably some of our processes require the synergism of both the physical and chemical aspects of the discharge, thus foiling any attempt at neat categorization on our part.

Unfortunately, practical glow discharges are rather complex environments, particularly the chemical discharges used in plasma etching and deposition, and they are far from being well understood. So before we launch into the confusing (and sometimes conflicting) detail of specific discharges, let's look at some more collision phenomena, which are common to all of the glow discharge processes covered in this book. We shall also see the usefulness of the ideas of collision cross-section, and of electron volts as energy units.

## COLLISION CROSS-SECTION

Before we look further at collision processes, let's examine an alternative to the mean free path concept that we established in the last chapter, and see why it isn't such a useful parameter after all.

Consider, in Figure 2-1, an electron approaching a volume of gas contained in a slab  $\Delta x$  thick and cross-sectional area  $A$ . Except for the very slowest electrons, the atoms of the gas move so much more slowly than the electrons that we can assume the atoms are relatively stationary. If the gas density is  $n$  molecules per unit volume and the effective collision area of each molecule is  $q$ , then the probability of a collision in that slab is  $n \Delta x q$  — the fraction of the cross-sectional area occupied by molecular targets. So the collision probability is  $nq$  per unit length. This tacitly assumes that  $n \Delta x q \ll 1$ , so that none of the 'targets' overlap. We can always assure this by making  $\Delta x$  vanishingly small and integrating. But at sufficiently low pressures the inequality is satisfied even for finite  $\Delta x$ .

It might at first appear that  $\lambda$  and  $q$  are simply related by  $nq = 1/\lambda$ . Although this would not be a simple relationship anyway, it also hides the real significance of the concept of *collision cross-section*, as the collision area is normally known. An electron approaching an atom sees the atom not as a solid ball but as an

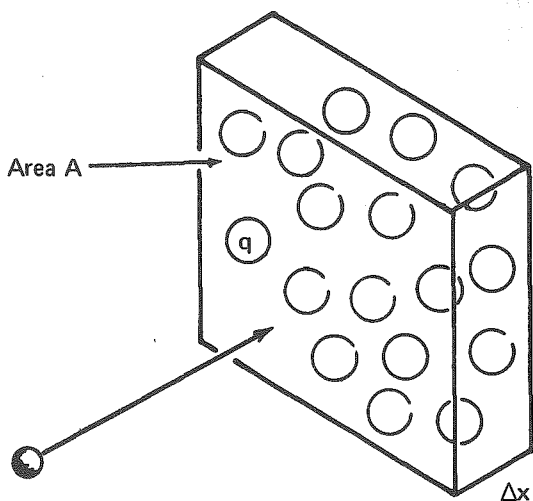


Figure 2-1. Probability of collision =  $\frac{n \Delta x q}{A} \Delta x = nq/\text{unit length}$

## ELASTIC AND INELASTIC COLLISIONS

assembly of electrons and ions in largely empty space. An analogy is that if the nucleus of the atom were represented in size by a cricket ball, then the electron orbits would be around the perimeter of the field. Probably the situation wouldn't be too different in baseball! The interaction between the primary electron and the electrons and ions of the atom take place via strong electrostatic forces, so the precise outcome depends on the detail of the approach of the electron. This introduces an element of probability or uncertainty into the interaction in contrast to the certainty of collision between two converging billiard balls (or elastically colliding atoms). This probability is implicit in our definition of collision cross-section  $q$ . It is also not surprising that  $q$  depends on approach velocity, and this is easily dealt with by making  $q$  a function of electron velocity or energy. This dependence can be intuitively rationalised in various ways, for example by arguing that the interaction time decreases with increasing velocity.

So it appears that collision cross-section is a more versatile parameter than mean free path  $\lambda$ , which is therefore conventionally reserved for elastic collisions between thermal molecules. And although we introduced the collision cross-section concept via electron-atom interactions, it's clearly of more general application.

## ELASTIC AND INELASTIC COLLISIONS

Collision processes can be broadly divided into elastic and inelastic types, according to whether the internal energies of the colliding bodies are maintained. Particles usually have two types of energy: kinetic energy due to their motion and equal to  $\frac{1}{2}mv^2$  for translational motion, and internal or potential energy which may be in the form of electronic excitation, ionization, etc.

An *elastic* collision is one in which there is an interchange of kinetic energy only. An *inelastic* collision has no such restriction, and internal energies change also.

In the last chapter, we established an energy transfer function:

$$\frac{4m_i m_t}{(m_i + m_t)^2}$$

which gives the maximum energy transferable in an elastic binary collision. As a consequence, the fraction of energy transferred from an electron to a nitrogen molecule was about  $10^{-4}$ . But now allow the collision to be inelastic, so that the molecule struck gains internal energy of  $\Delta U$  (Figure 2-2). Then, using almost the same equations as previously:

Momentum conservation

$$m_i v_i \cos \theta = m_i u_i + m_t u_t$$

Energy conservation

$$\frac{1}{2} m_i v_i^2 = \frac{1}{2} m_i (u_i^2 + v_i^2 \sin^2 \theta) + \frac{1}{2} m_t u_t^2 + \Delta U \quad (1)$$

Eliminating  $u_i$  as before gives

$$m_i v_i^2 = \frac{m_i}{m_t^2} (m_i v_i \cos \theta - m_t u_t)^2 + m_t u_t^2 + 2\Delta U \quad (2)$$

which simplifies to

$$2m_t u_t v_i \cos \theta = \frac{m_t}{m_i} (m_t + m_i) u_t^2 + 2\Delta U \quad (3)$$

$\Delta U$  and  $u_t$  are the only variables. To maximize  $\Delta U$ ,

$$2 \frac{d}{du_t} (\Delta U) = 2m_t v_i \cos \theta - \frac{m_t}{m_i} (m_t + m_i) 2u_t = 0$$

$$\text{i.e. } v_i \cos \theta = \frac{(m_t + m_i) u_t}{m_i}$$

Substituting back into (3), we obtain

$$2\Delta U = \left( \frac{m_t m_i}{m_t + m_i} \right) v_i^2 \cos^2 \theta$$

Hence the fraction of the kinetic energy of the first particle that can be transferred to the internal energy of the second, has a maximum value of

$$\frac{\Delta U}{\frac{1}{2} m_i v_i^2} = \frac{m_t}{m_t + m_i} \cos^2 \theta$$

So whereas the maximum elastic energy transfer from an electron to a nitrogen molecule was only 0.01%, by inelastic means this may rise to more than 99.99%, since when  $m_t \gg m_i$ , this *inelastic energy transfer function* tends to 1.

From equation (3), it seems that the fractional kinetic energy transfer is

$$\frac{\frac{1}{2} m_t u_t^2}{\frac{1}{2} m_i v_i^2} = \frac{m_t u_t^2}{m_i} \left( \frac{2m_t u_t}{\frac{m_t}{m_i} (m_t + m_i) u_t^2 + 2\Delta U} \right)^2$$

Excluding the cases when  $\Delta U$  can be negative, this function has a maximum value when the denominator has a minimum value given by  $\Delta U = 0$ ; then the fractional energy transfer reverts to the  $4m_i m_t / (m_i + m_t)^2$  value as expected. So even

though a good deal of potential energy can be transferred when  $m_i \ll m_t$ , it is still impossible to transfer any significant amount of kinetic energy.

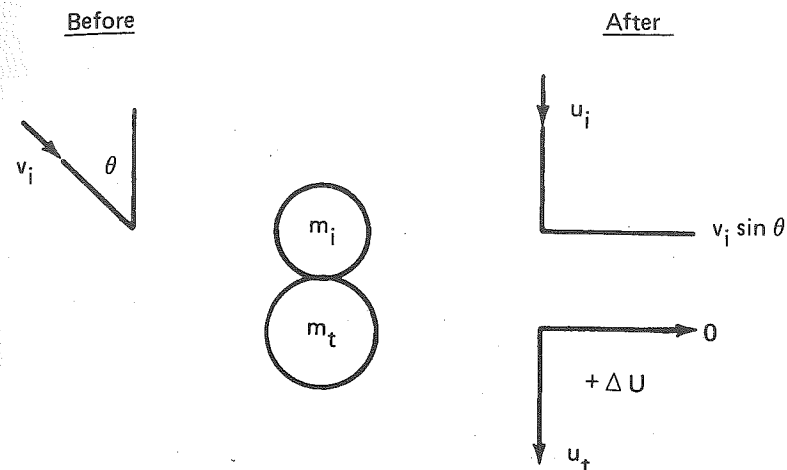


Figure 2-2. Kinetics of an inelastic collision

## THE MAIN COLLISION PROCESSES

The gas phase environment of a glow discharge contains electrons, various types of ions, neutral atoms and molecules, and photons. In principle we should consider collisions between all possible pair permutations, but fortunately some collisions are more important than others in the glow discharge environments that we are considering in this book. Collisions involving electrons are dominant in determining the macroscopic behaviour of the glow discharge, and therefore we begin by considering these.

### Electron Volts

Electrons are, of course, readily accelerated or decelerated by electric fields. If an electron is accelerated between 2 points of potential difference  $X$  volts, then by definition it loses  $eX$  joules of potential energy and gains an equivalent amount of kinetic energy;  $e$  is the electron charge of  $1.6 \cdot 10^{-19}$  coulombs. This  $eX$  joules of kinetic energy is also conveniently referred to as  $X$  *electron volts* or  $X$  eV, and so:

$$1\text{eV} = 1.6 \cdot 10^{-12} \text{ ergs}$$

This derived energy unit of electron volts turns out to be generally useful and can be applied to neutral as well as other charged particles.

### Elastic Collisions

The simplest collisions are elastic, so that kinetic energy is conserved. But since the electron and any atom have such different masses, we know from the energy transfer function  $4m_i m_t / (m_i + m_t)^2$  that the transfer of energy is negligible; so the electron just changes direction without significantly changing speed (Figure 2-3). Where the electron is moving in an electric field, elastic collisions generally have the effect of restricting its velocity in the direction of the field, in the same way that drift velocity of a conduction electron in a solid is restricted by lattice collisions. In both cases, the colliding atom is virtually unaffected. We can use the collision cross-section concept to describe the probability of elastic collision, as in Figure 2-4 which shows how the chance of an electron being scattered in argon depends on the energy of the electron. To translate the cross-section into something more easily considered, it appears from Figure 2-4 that the elastic cross-section for an argon atom to a 15 eV electron is about  $2.5 \cdot 10^{-15} \text{ cm}^2$ . So, at 10 mtorr when there are  $3.54 \cdot 10^{14}$  atoms/cc, the probability of elastic collision for a 15 eV electron is 0.89/cm.

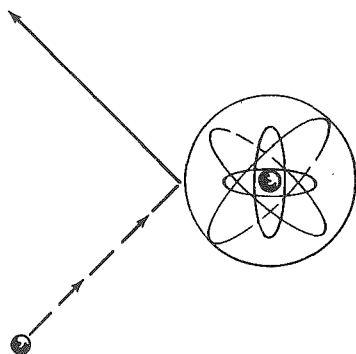


Figure 2-3. Electron - atom elastic collision

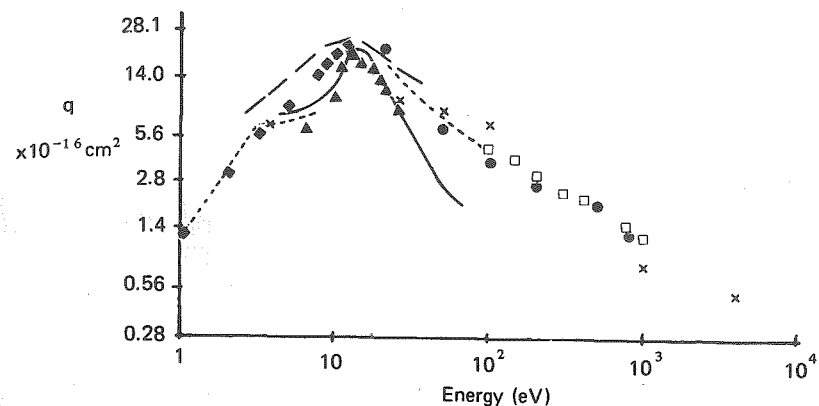
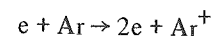


Figure 2-4. Cross-section for elastic scattering of electrons in argon. From DuBois and Rudd 1975; includes data from various authors

### Ionization

All other types of electron collisions are inelastic. The most important of these in sustaining the glow discharge is *electron impact ionization* (Figure 2-5) in which the primary electron removes an electron from the atom, producing a positive ion and two electrons, e.g.



The two electrons produced by the ionizing collision can then be accelerated by an electric field until they, too, can produce ionization. It is by this multiplication process that a glow discharge is maintained.

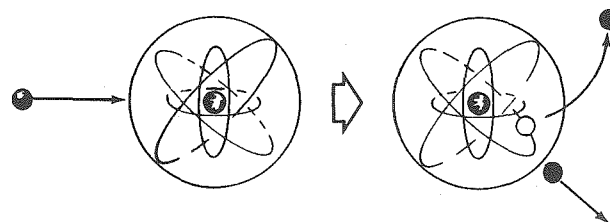


Figure 2-5. Electron impact ionization

There is a minimum energy requirement for this ionization process to occur, equal to the energy to remove the most weakly bound electron from the atom, and this is known as the *ionization potential*; for xenon this has a value of 12.08 eV. Below this threshold energy, the ionization cross-section is clearly zero, but rises as soon as the electron exceeds the ionization potential (Figure 2-6). The energy dependence of the ionization cross-section for xenon over a rather larger electron energy range is shown in Figure 2-7. This is fairly typical for the inert gases, quickly rising above the threshold to a maximum around 100 eV and then falling. Cross-sections for other noble gases are shown in Figure 2-8. Note that this figure gives the cross-sections in units of  $\pi a_0^2$  rather than  $\text{cm}^2$ . In this unit,  $a_0$  is the radius ( $0.53 \cdot 10^{-8} \text{ cm}$ ) of the first Bohr orbit of hydrogen;  $\pi a_0^2$  is the area of a hydrogen atom and has the value  $8.82 \cdot 10^{-17} \text{ cm}^2$ , a unit of useful size.

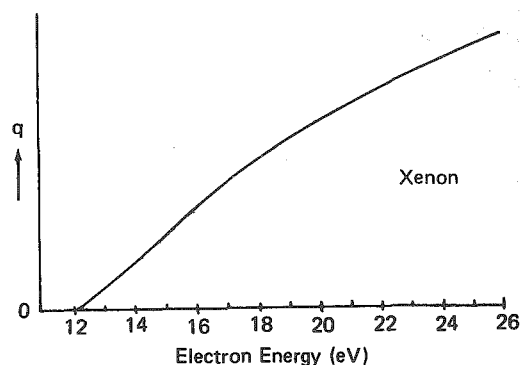


Figure 2-6. Ionization cross-section for xenon near threshold (Rapp and Englander-Golden 1965)

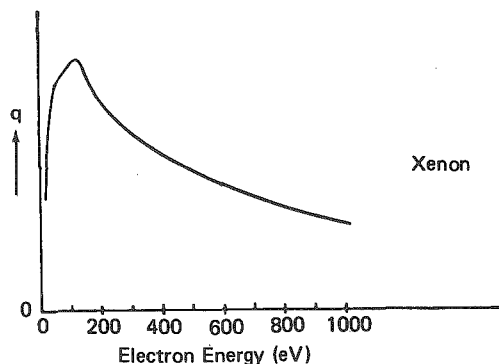


Figure 2-7. Ionization cross-section for xenon, 0-1000 eV (Rapp and Englander-Golden 1965)

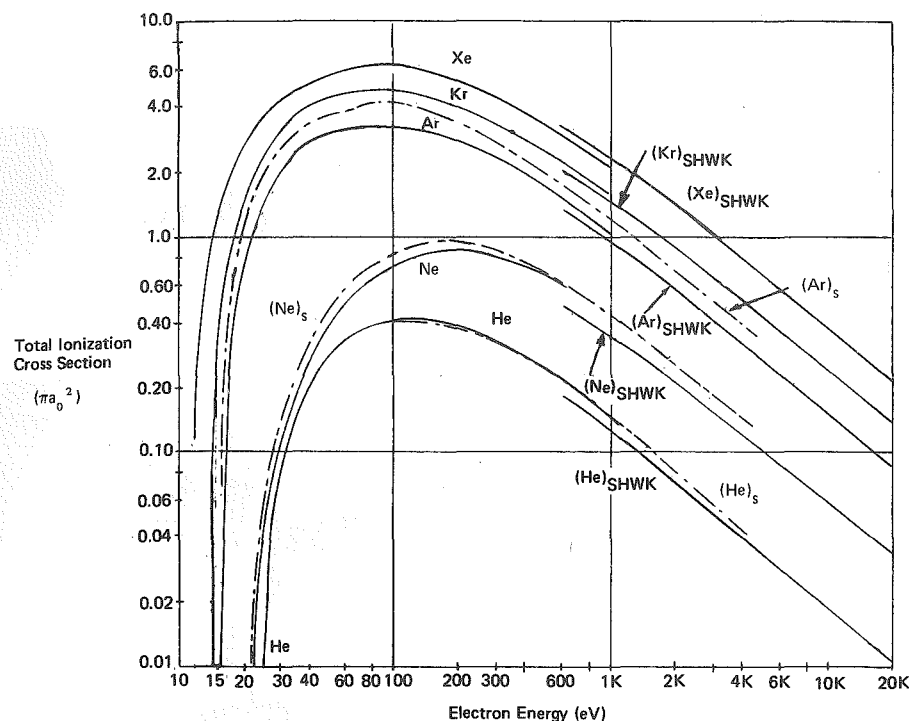


Figure 2-8. Ionization cross-sections of the noble gases (from Rapp and Englander-Golden 1965; includes data from (S) Smith 1930 and (SHWK) Schram et al. 1965. Similar values for Ar, He and Ne have been obtained by Fletcher and Cowling 1973); n.b.  $\pi a_0^2 = 8.82 \times 10^{-17} \text{ cm}^2$

It is not only by electron impact that ionization is produced. In principle, the ionization could be due to any suitable energy input, and the possibilities in the discharge must therefore include thermal and photon activation. In the present context, 'thermal activation' means energy received by impact with neutral ground state gas atoms or with the atoms of the walls, and for our 'cold' plasmas, the temperature does not greatly exceed ambient. *Photoionization* can be significant, however. In order to relate the two relevant commonly used photon parameters of wavelength and energy, a useful and reasonably good approximation is:

$$1\text{eV} \equiv 12345 \text{ \AA}$$

since

$$E = h\nu = \frac{hc}{\lambda}$$

The photoionization cross-section for argon, shown in Figure 2-9, exhibits a threshold at 15.8 eV as expected, rising rapidly to a cross-section of about  $3.7 \times 10^{-17} \text{ cm}^2$  before decreasing for higher photon energies, with further discontinuities as fresh ionization thresholds are encountered. By comparison, note (Figures 2-8 and 2-6) that the electron impact cross-section around threshold is virtually zero, but rises to a maximum of about  $2.6 \times 10^{-16} \text{ cm}^2$  at around 100 eV.

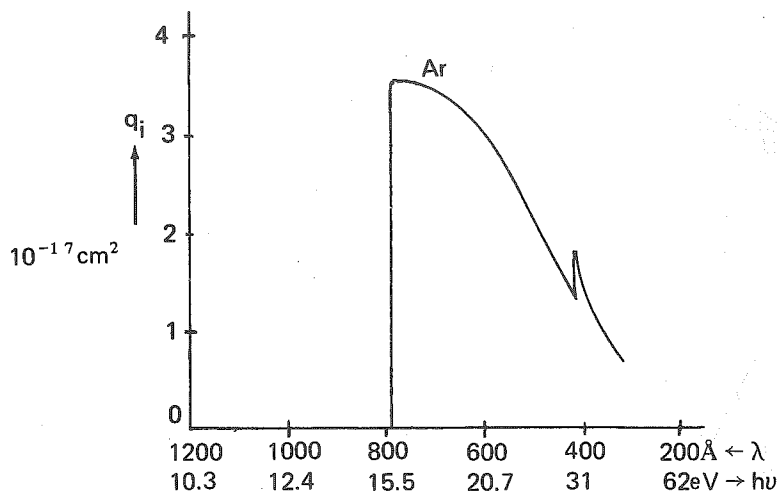


Figure 2-9. Photoionization cross-section of argon (Weissler 1956)

Although the photoionization cross-section seems to decrease to rather small values, this does not mean that there is very little ionization. The reason is two-fold: firstly, the excess energy (between the incident photon and the relevant ionization energy) appears mostly as kinetic energy of the emitted electron, since little kinetic energy can be transferred to the gas atom as we know from the energy transfer function, and this energetic electron can now cause further ionization; secondly, the 'hole' in the atom left by the ionization process will be filled by an electron transition from a higher level and the accompanying photon emission usually causes more ionization – and hence the ejection of more electrons – on its way out of the atom (– the Auger effect is an example). Similar arguments can be used to explain photoelectron emission from chamber walls and all internal surfaces, including electrodes. As a result, one would expect a large proportion of photon energy to lead ultimately to ionization. Although

## THE MAIN COLLISION PROCESSES

some photons will be lost from the chamber through transparent windows or through quartz chamber walls, most windows do not transmit below about 2500 Å, i.e. above about 5 eV. The maximum photon energies found in plasma processes correspond to about the peak-to-peak driving voltage used, i.e. about 1000 eV, and are due mostly to ion and electron impact on chamber surfaces. These energetic photons will penetrate on hitting another surface, so that electrons produced may not be able to escape; in this case the photon energy is dissipated in heat.

There are two other ionization processes frequently occurring in the glow discharge, and these are described below (ion-neutral collisions, and metastable-neutral collisions).

### Excitation

In the ionization process, a bound electron in an atom is ejected from that atom. A less dramatic transfer of energy to the bound electron would enable the electron to jump to a higher energy level within the atom with a corresponding quantum absorption of energy. This process is known as *excitation*, and as with ionization can result from electron impact excitation (Figure 2-10), photo-excitation, or thermal excitation, although the latter is rare in 'our' cold discharges.

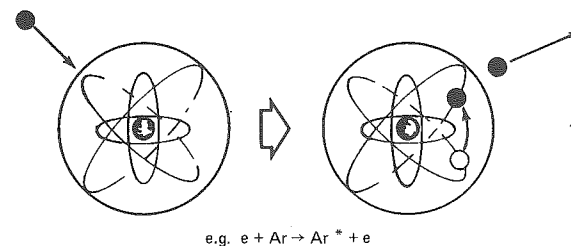


Figure 2-10. Electron impact excitation

The excited state is conventionally represented by an asterisk superscript, e.g.  $\text{Ar}^*$ . As with ionization, there is a minimum energy for excitation to occur. The value of the *excitation potential* for argon is 11.56 eV, somewhat less than the ionization potential, as would be expected since excitation raises an electron to a higher (less tightly-bound) shell, and ionization completely removes the electron from the atom. In an exciting collision, the primary electron loses kinetic energy equal to the excitation potential and will also be deflected.

In Figure 2-11, the energy dependencies of the electron excitation cross-sections of the 2p levels of argon are shown. These rise from a threshold at 12.90 eV to a maximum at 21 eV electron energy, of  $4 \times 10^{-17} \text{ cm}^2$ .

Figure 2-12 shows the excitation cross-section for atomic hydrogen. Note, by comparison, the corresponding cross-section in Figure 2-13 for molecular hydrogen, which has a much lower threshold due to the possibilities of vibrational and rotational excitation.

As with ionization, excitation can also be caused by photons; the cross-sections are of the same order as the ionization cross-sections discussed earlier.

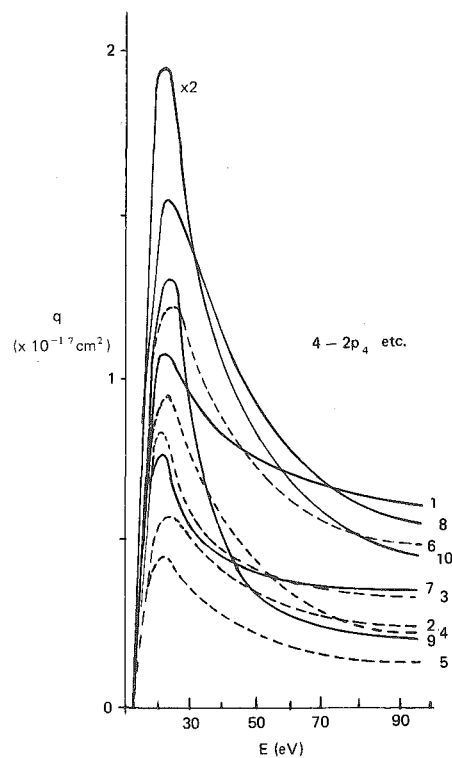


Figure 2-11. Excitation cross-sections of the 2p levels of argon (Zapesochnyi and Feltsan 1966)

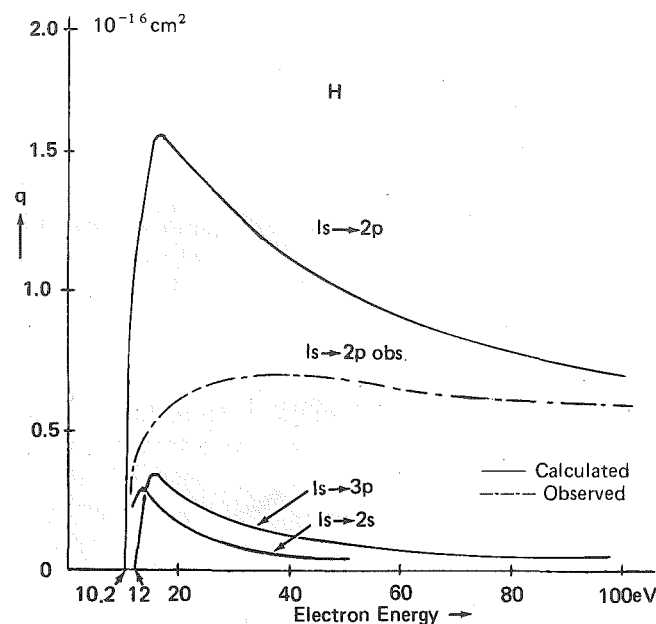


Figure 2-12. Excitation cross-section for electrons in atomic hydrogen (von Engel 1965)

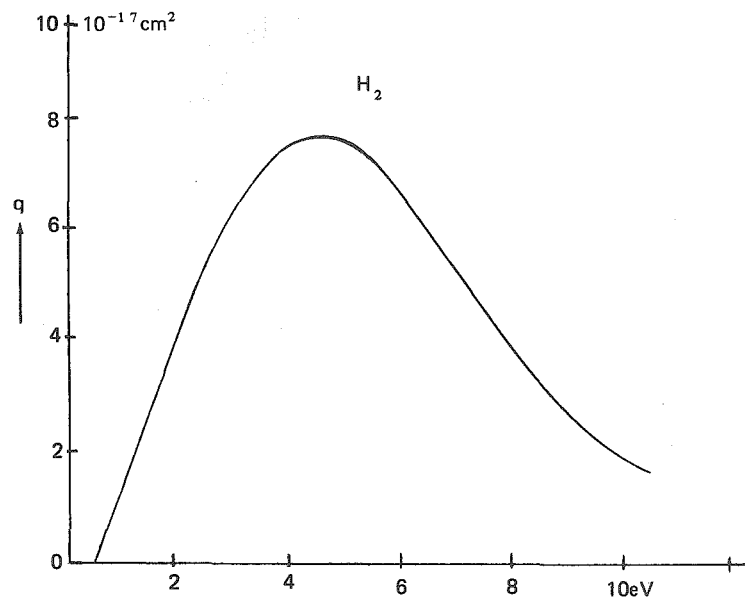


Figure 2-13. Excitation cross-section for electrons in molecular hydrogen (Frost and Phelps 1962)

## Relaxation

One of the immediately self-evident features of a glow discharge is that it glows! This glow is due to the *relaxation* or de-excitation of electronically excited atoms and molecules — the inverse of the excitation process just discussed. These excited states are rather unstable and the electron configuration soon returns to its original (ground) state in one or several transitions, with lifetimes varying enormously from nanoseconds to seconds. Each transition is accompanied by the *emission* of a photon of very specific energy, equal to the difference  $\Delta E$  in energy between the relevant quantum levels (Figure 2-14). Our eyes are sensitive only to wavelengths between about 4100 Å (violet) and 7200 Å (red), corresponding to electron transitions of 3.0 eV and 1.7 eV respectively, but with suitable detection equipment, photons from deep uv (atomic transitions) to far infra-red (molecular vibrational and rotational transitions) can be detected. The technique of optical emission spectroscopy is thus very useful for detecting and determining the presence of various atoms in the glow. Figure 2-15 shows the emission spectrum from a glow discharge of  $\text{CF}_4 + \text{O}_2$ , a gas mixture commonly used in plasma etching.

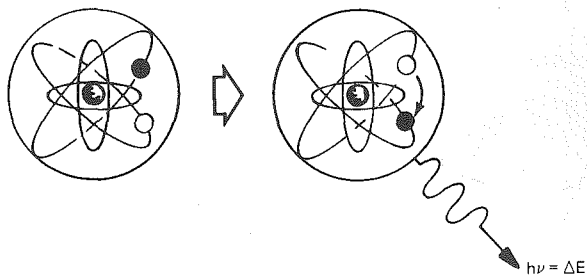
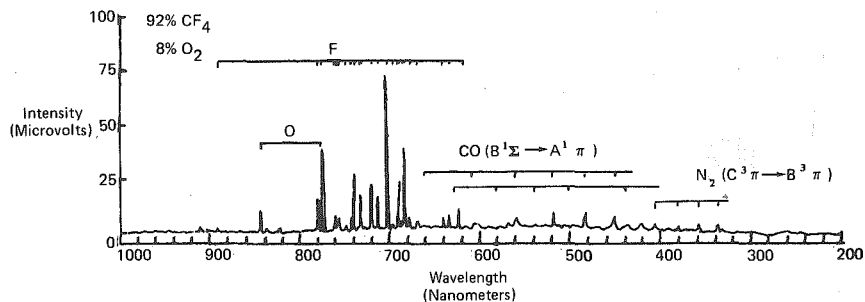


Figure 2-14. Relaxation (or de-excitation)

Figure 2-15. Optical emission from a discharge of  $\text{CF}_4 + \text{O}_2$  (Harshbarger et al. 1977)

## THE MAIN COLLISION PROCESSES

## Recombination

Just as relaxation is the inverse of excitation, so recombination is to ionization — an electron coalesces with a positive ion to form a neutral atom (Figure 2-16). However, there is a problem:

Assume (Figure 2-17) that the electron has a mass  $m$  and has a velocity, relative to the ion of mass  $M$ , of  $v$  before recombination. Let their joint velocity after coalescence be  $u$ . The potential energy of the atom has decreased by  $U_i$ , the relevant ionization energy. Then, to continue our earlier applied mathematical exercises:

Conservation of momentum:

$$mv = (m + M)u$$

Conservation of energy:

$$\frac{1}{2}mv^2 = \frac{1}{2}(m + M)u^2 - U_i$$

Therefore, eliminating  $v$ ,

$$\frac{1}{2}m \left( \frac{m + M}{m} \right)^2 u^2 = \frac{1}{2}(m + M)u^2 - U_i$$

which yields

$$u^2 = - \frac{2U_i m}{(m + M)M}$$

but since  $U_i$ ,  $m$ , and  $M$  are all positive, this yields only an unreal solution for  $u$ . This means that, in general, a 2 body coalescence is just not possible. In practice, allowing for Heisenberg, this type of recombination is very unlikely. But recombination must occur somehow, because otherwise the ion and electron densities in any ionizing environment, such as a glow discharge, would continuously increase and this is contrary to experience. Some more subtle recombination processes therefore may take place:

**3 Body Collision:** A third body takes part in the collision process, and this third body allows the recombination process to simultaneously satisfy the conservation requirements of energy and momentum (Figure 2-18). The third body is often a wall, ubiquitous in our plasma processes, or it may be another gas atom. The probability of the gas atom taking part in the process will increase with increasing pressure; the wall is always there.



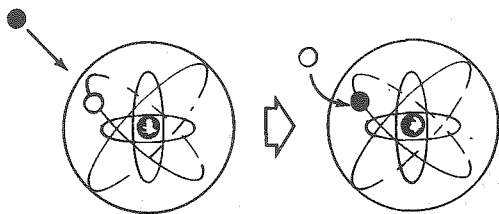


Figure 2-16. Recombination

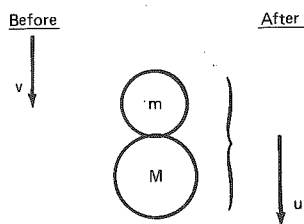


Figure 2-17. Kinetics of recombination

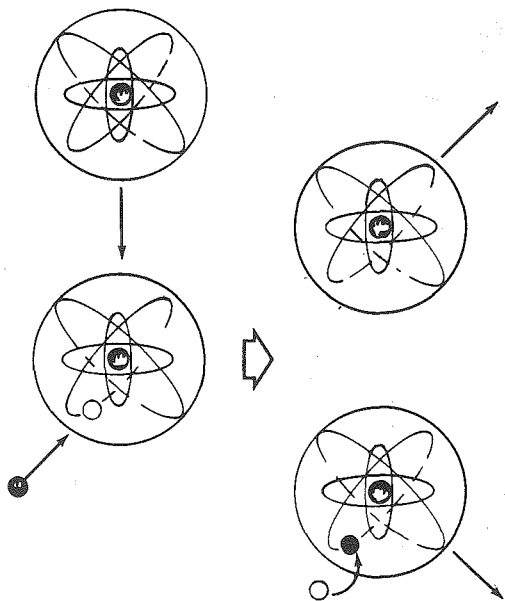


Figure 2-18. 3-body recombination

## SOME OTHER COLLISION PROCESSES

*In a Two Stage Process:* The electron <sup>U<sub>em</sub></sup> attaches to a neutral to form a negative ion. Whilst not very likely, this process has  $U_i$  negative and so is possible. The negative ion then collides with a positive ion. The electron transfers and two neutrals are formed (Figure 2-19). The number of collisions between an electron and an atom before forming a negative ion depends on its electronegativity (its affinity for electrons) and ranges from about  $10^3$  for molecular chlorine to  $\infty$  for the noble gases.

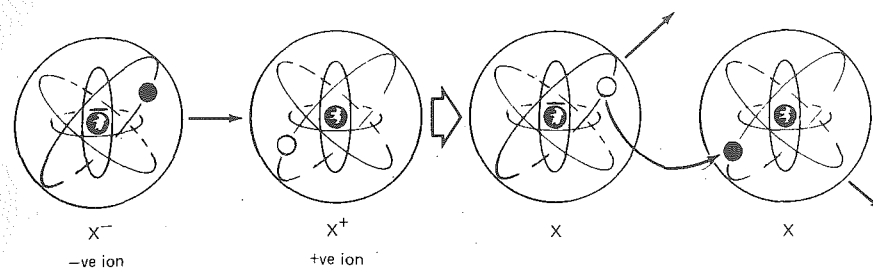


Figure 2-19. Ion-ion recombination

*Radiative Recombination:* The excess energy in the coalescence process of recombination is carried away by radiation (Figure 2-20). This is really another type of 3 body recombination.

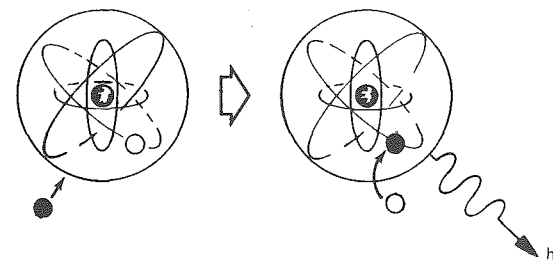


Figure 2-20. Radiative recombination

## SOME OTHER COLLISION PROCESSES.

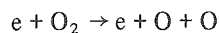
The four basic inelastic processes that were considered in the first part of this chapter – ionization and recombination, excitation and relaxation – are the inevitable ingredients of a glow discharge. We can understand the basic phenomena of a discharge by considering just these four inelastic processes and the reader may wish to omit the rest of this section on the first time through.

But as we said at the beginning of the chapter, there are many other collisional processes and some of these are important under some circumstances. We'll consider now the more relevant of these.

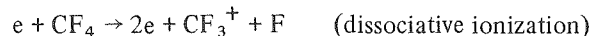
### Dissociation

The process of *dissociation* is the breaking apart of a molecule. An oxygen molecule can be dissociated into two oxygen atoms, but an atomic gas such as argon cannot be dissociated at all.

As with the other inelastic processes we have been studying, dissociation can in principle be accomplished with any energy in excess of the dissociation threshold, i.e. the relevant bond strength in the molecule. In glow discharges, electron impact dissociation is common:



A normal result of dissociation is an enhancement of chemical activity since the products are usually more reactive than the parent molecule. We shall see in Chapter 7 how such enhancement of activity is used to oxidize photoresists in the *plasma ashing* process. We shall also see that dissociation may or may not be accompanied by ionization:



There are different probabilities, and hence different cross-sections, for each of these processes.

### Electron Attachment

There is a possibility that an electron colliding with an atom may join on to the atom to form a negative ion. This process is known as *electron attachment*. The noble gases, including argon, already have filled outer electron shells and so have little or no propensity to form negative ions. Halogen atoms, however, have an unfilled state in their outer electron shells; they have high electron affinities and so readily form negative ions. Figure 2-21 shows the rate of production of  $SF_6^-$  and  $SF_5^-$  negative ions by attachment as a function of the electron energy, from  $SF_6$  gas. The production of  $SF_5^-$  in this way is known as *dissociative attachment* ( $e + SF_6 \rightarrow SF_5^- + F$ ). It can be seen that the  $SF_6^-$  ion is formed more effectively by the attachment of electrons of almost zero energy. This is another manifestation of the problem of simultaneously satisfying energy and momentum conservation ("Recombination"). Certain interpretations are necessary to convert these production rates into collision cross-sections, but it seems (Massey 1969) that the cross-section may exceed  $10^{-15} \text{ cm}^2$ , with the resulting ion being

### SOME OTHER COLLISION PROCESSES

metastable with a lifetime greater than  $10^{-6}$  secs. Massey also cites several references to other halogen-containing gases; gases of this type are of importance in plasma etching.

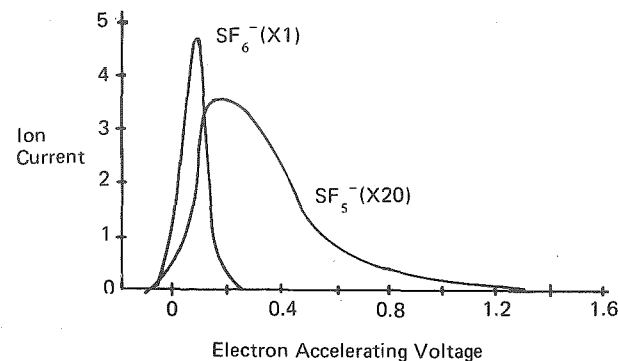


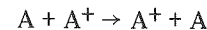
Figure 2-21. The  $SF_6^-$  and  $SF_5^-$  currents obtained by Hickam and Fox (1956) in their mass spectrometric studies of  $SF_6$ .

### Ion-Neutral Collisions

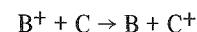
Ions and neutrals can collide with each other elastically, or inelastically to either exchange charges or cause further ionization.

### Charge Transfer

The probability of a collision leading to the exchange of charge, generically known as *charge transfer*, is usually greater for atomic ions moving in parent atoms (*symmetrical resonant charge transfer*), e.g.



(Figure 2-22) or similarly for molecular ions moving in parent molecular gases, than in charge exchange between unlike systems, e.g.



which is known as *asymmetric charge transfer* and tends to be less efficient (Figure 2-23). Figure 2-24 shows both the elastic and symmetric charge transfer cross-sections for noble gas ions in their parent gases.

Symmetrical charge exchange in a field-free glow region is rather unimportant since there is, effectively, only a momentum exchange. But both types of charge transfer become important in a sheath region, where they have the effect of changing the energy distribution of ions and neutrals on the electrode (Chapter 4, "Collisions in the Sheath").

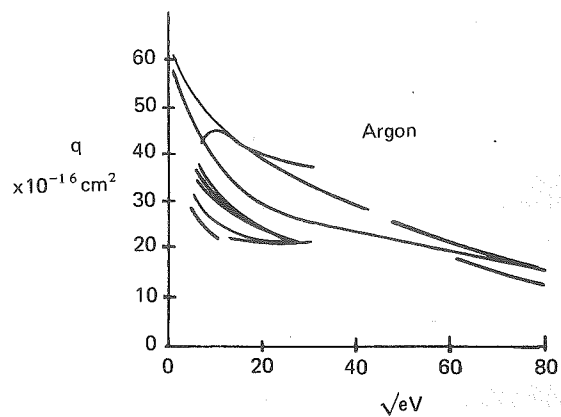


Figure 2-22. Cross-sections for resonance charge transfer of  $\text{Ar}^+$  on Ar, as shown in McDaniel 1964; data from several authors

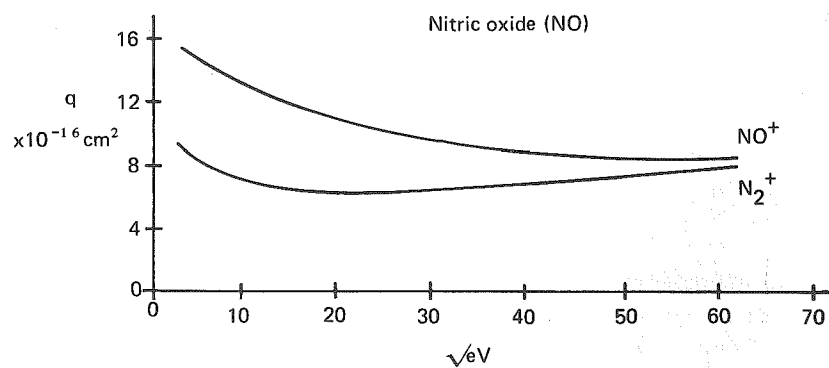


Figure 2-23. Charge transfer cross-sections for  $\text{NO}^+$  and  $\text{N}_2^+$  ions in nitric oxide (Stebbing et al. 1963)

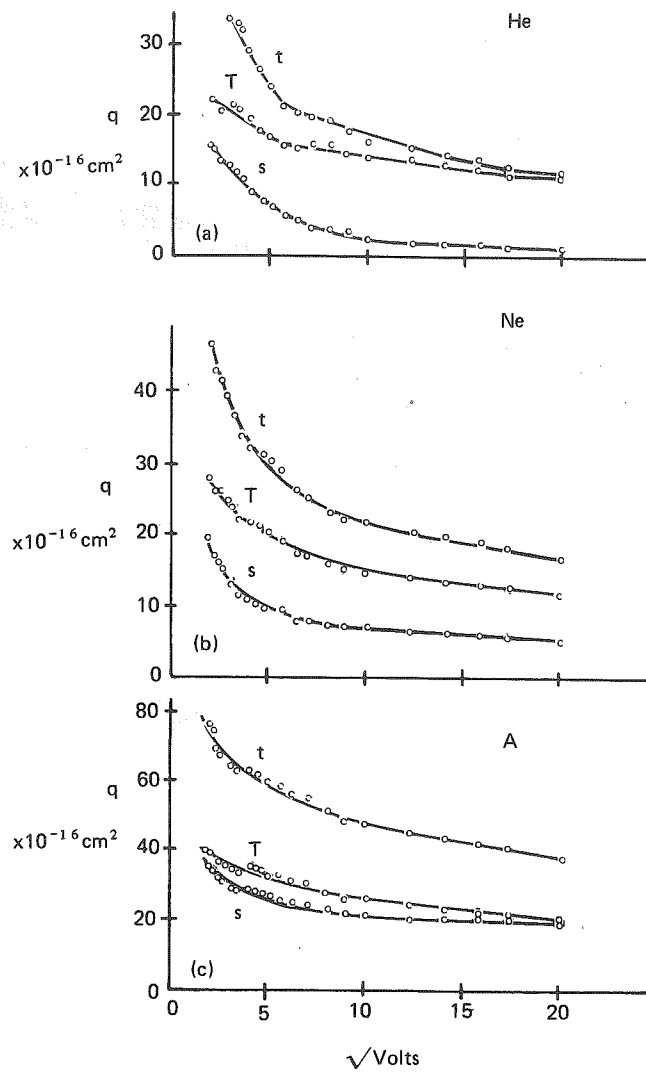


Figure 2-24. Experimental values for scattering cross-sections of ions in He, Ne and Ar;  $q$  is in units of  $10^{-16} \text{ cm}^2$ . The symbol  $s$  refers to elastic scattering,  $T$  to charge transfer, and  $t$  to the sum of  $s$  and  $T$ .  
 (a)  $\text{He}^+$  on He; Cramer and Simons 1957  
 (b)  $\text{Ne}^+$  on Ne; Cramer 1958.  
 (c)  $\text{Ar}^+$  on Ar; Cramer 1959.

### Ionization By Ion Impact

Just as ionization can be produced by photon bombardment, so it can also be produced by fast ion or fast atom bombardment, provided the incident particles have enough energy. Figure 2-25 shows the energy dependence of the ionization cross-section of several ions in their parent gases, whilst Figure 2-26 shows corresponding values for fast neutral atoms. Note that the cross-sections are of the order of  $10^{-16}$  cm<sup>2</sup> (see also McDaniel 1964, p. 276). We shall consider the potential significance of these processes in glow discharges in Chapter 4.

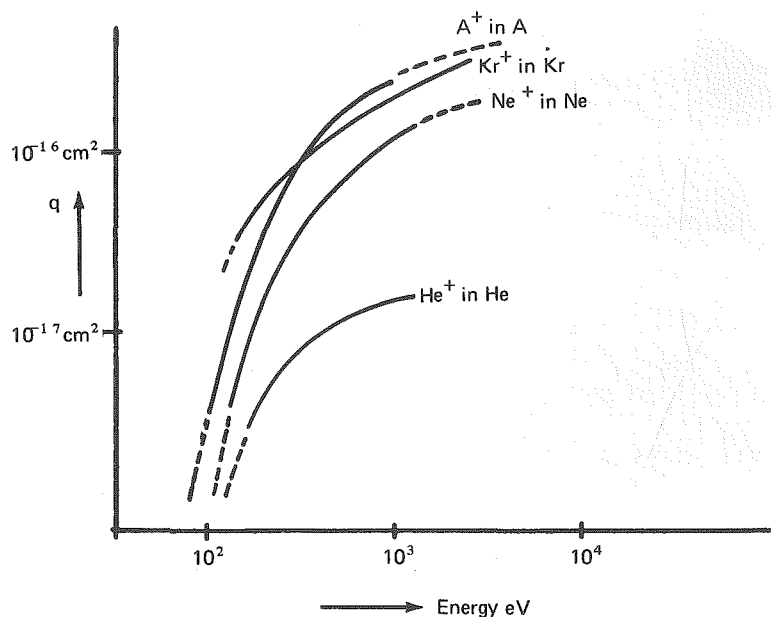


Figure 2-25. Ionization cross-sections of ions in their parent gases. Actually these values are too high because the ionizing effects of the secondary electrons produced have not been subtracted. The curve for Ar<sup>+</sup> is uncertain. (From von Engel 1965; includes data from Rostagni 1934, 1938 and Wien 1927)

### Ion Chemistry

The subject of ion-atom interactions is also the basis of *ion chemistry*. I am not qualified to discuss this subject. It is interesting how atoms can completely change their chemical nature by becoming ionized. Argon, for example, is a noble unreactive gas because it has a closed outer shell configuration. However, on being ionized, it loses an electron and acquires the electron shell configura-

tion of chlorine, becoming similarly reactive. This is presumably why complex ions such as ArH<sup>+</sup> are observed in sputtering glow discharges (Coburn and Kay 1971), being the ion equivalent of HCl.

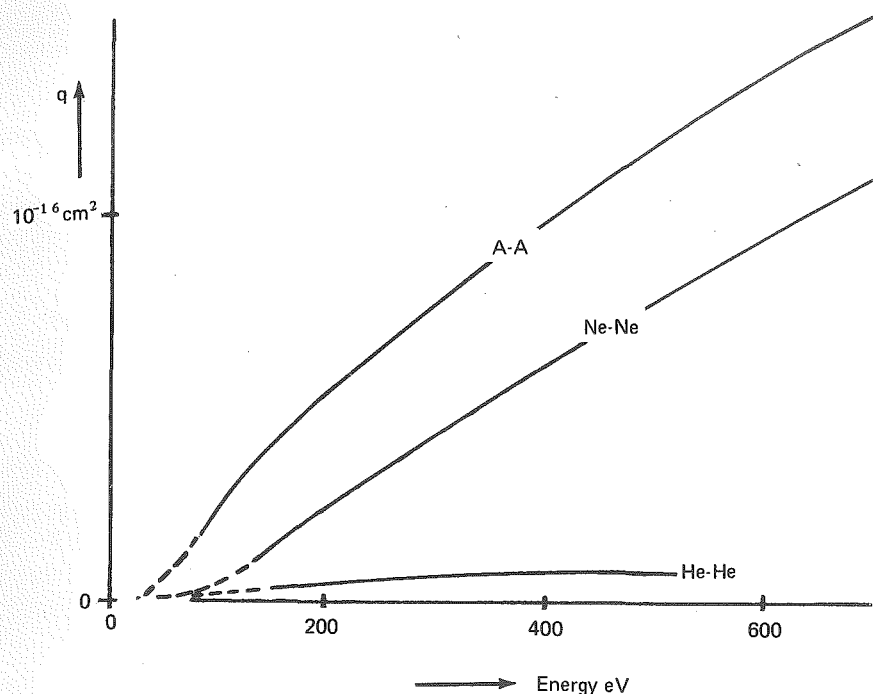


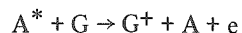
Figure 2-26. Ionization cross-section of fast atoms in their parent gas. Again secondary electron effects should be accounted for. (From von Engel 1965, including data from Rostagni 1934, 1938)

### Metastable Collisions

The probability of collisions involving excited atoms depends on the density of the excited atoms, and hence on their lifetime. Some excited atoms have very long lifetimes (1 mS - 1 s, cf. lnS for resonant states) and these are known as *metastable* excited atoms; they arise because the selection rules forbid relaxation to the ground state, or in practice, make such a transition rather unlikely. All of the noble gases have metastable states; argon has metastables at 11.5 eV and 11.7 eV.

*Metastable – Neutral Collisions*

When a metastable atom collides with a neutral, the neutral can become ionized if its ionization energy is less than the excitation energy of the excited atom:

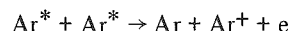


This is known as *Penning Ionization*.

Coburn and Kay (1971) demonstrated the Penning ionization effect by sputtering a europium oxide target containing a small amount of iron, in both neon and argon discharges.  $\text{Eu}^+$  ( $eV_i = 5.7 \text{ eV}$ ) and  $\text{Fe}^+$  ( $eV_i = 7.8 \text{ eV}$ ) were observed in both gases, but  $\text{O}^+$  ( $eV_i = 13.6 \text{ eV}$ ) was observed only in the neon discharge. Argon metastables are at 11.5 eV and 11.7 eV, whereas neon metastables are at 16.6 eV and 16.7 eV.

*Metastable – Metastable Ionization*

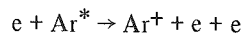
Lounsbury (1969) has pointed out that two metastable argon atoms, each of energy 11.55 eV, have sufficient energy that their collision could result in the ionization (threshold 15.76 eV) of one of the pair:



Using emission spectroscopy techniques, Lounsbury concluded that this was not a major ionization mechanism in an rf discharge. The metastable density is probably  $\sim 10^{10} \text{ cm}^{-3}$  (Ekstein et al. 1975). Assuming that the mean free path for argon metastable encounters is the same as for argon ground state atoms of the same density, then there will be only about  $10^{11}$  metastable-metastable encounters/ $\text{cm}^3$ , much less than the electron impact ionization rate in a self-sustained discharge.

*Electron – Metastable Ionization*

Just as a ground state atom can be ionized by electron impact, so can a metastable:



The major difference between the ionization of a metastable and of a ground state is that the threshold for the latter is 15.76 eV, whilst for the former it would be only 4.21 eV, assuming an 11.55 eV metastable. So although there will usually be many fewer metastables than ground state atoms in our glow discharges, there will be many more electrons capable of ionizing the metastables than of ionizing the ground state atoms. Unfortunately, there seems to be little known about the ionization cross-section of the metastables. We shall return to consider their contribution to glow discharges in Chapter 4.

## TOTAL COLLISION CROSS-SECTION

## TOTAL COLLISION CROSS-SECTION

As we have seen, an electron travelling through a gas may take part in several processes: elastic scattering, excitation, ionization, recombination, attachment. There is a certain probability for each of these processes to take place, expressed as a collision cross-section. But since each cross-section is a probability, then the chance of *any* one of these processes taking place is just a sum of the individual probabilities. So there is a *total* collision cross-section which is the sum of the individual cross-sections, and is a measure of, for example, an electron being scattered elastically or inelastically. Figure 2-27 shows the total collision cross-sections for electrons in the noble gases. For electrons of 16 eV in argon, just above the ionization threshold, the total cross-section is about  $23 \pi a_0^2$ , i.e. about  $2 \cdot 10^{-15} \text{ cm}^2$ . So, in argon at 50 mtorr ( $n = 1.8 \cdot 10^{15} \text{ atoms/cc}$ ), the probability of these electrons being scattered is about 0.4 per mm path length.

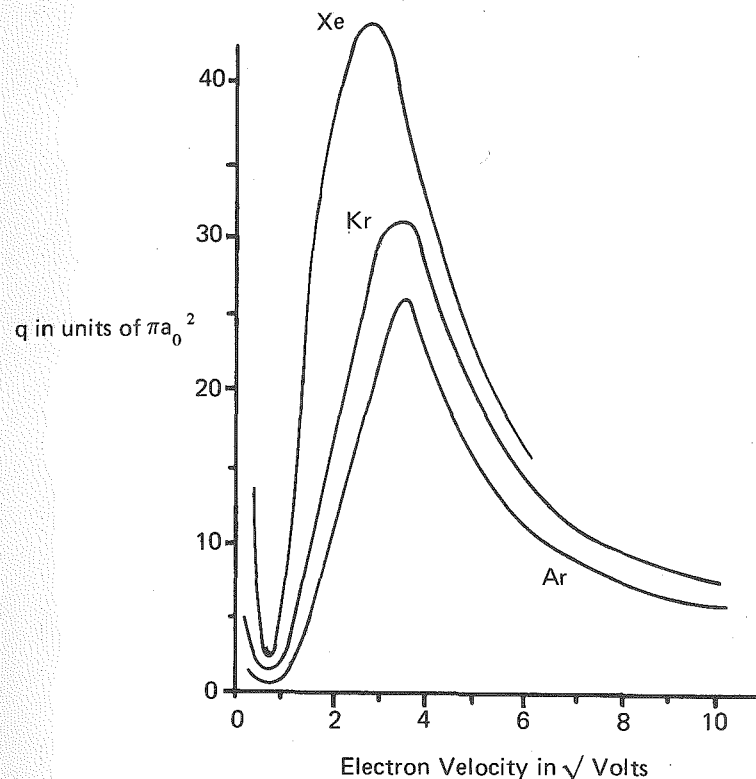
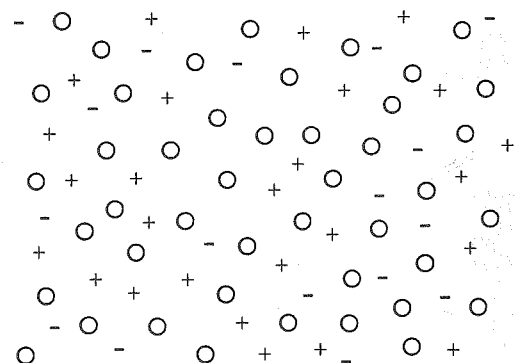


Figure 2-27. Total collision cross-section for electrons in the noble gases (Massey and Burhop 1969).

## PLASMA

We have now reached the stage where we can begin to consider a simple plasma consisting of positive ions and negative electrons in a sea of neutral atoms (Figure 2-28). Ion-electron pairs are continuously created by ionization and destroyed by recombination, as we have seen above. Since these processes are always pairwise, the space occupied remains charge neutral. The electron impact process which leads to ionization is also likely to lead to excitation and the subsequent relaxation of the atom leading to photon emission is another common feature of the plasma. In the next chapter, we shall investigate some of the properties of this plasma.



○ Neutral Atoms  
 - Negative Electrons  
 + Positive Ions

Figure 2-28. Plasma

## REFERENCES

## REFERENCES

- S. C. Brown, *Introduction To Electrical Discharges In Gases*, Wiley, New York and London (1966)
- J. W. Coburn and E. Kay, *Appl. Phys. Letters* **18**, 10, 435 (1971)
- W. H. Cramer and J. M. Simons, *J. Chem. Phys.* **26**, 1272 (1957)
- W. H. Cramer, *J. Chem. Phys.* **28**, 688 (1958)
- W. H. Cramer, *J. Chem. Phys.* **30**, 641 (1959)
- R. D. DuBois and M. E. Rudd, *J. Phys. B: Atom. Molec. Phys.* **8**, 9, 1474 (1975)
- A. von Engel, *Ionized Gases*, Oxford University Press, London and New York (1965)
- E. W. Ekstein, J. W. Coburn, and Eric Kay, *Int. Jnl. of Mass Spec. and Ion Physics* **17**, 129 (1975)
- J. Fletcher and I. R. Cowling, private communication (1973)
- L. S. Frost and A. V. Phelps, *Phys. Rev.* **127**, 1621 (1962)
- W. R. Harshbarger, R. A. Porter, T. A. Miller, and P. Norton, *Applied Spectroscopy* **31**, 3, 201 (1977)
- W. M. Hickam and R. E. Fox, *J. Chem. Phys.* **25**, 642 (1956)

H. S. W. Massey and E. H. S. Burhop, *Electronic and Ionic Impact Phenomena*, Vol. 1, Oxford University Press, London and New York (1969)

H. S. W. Massey, *Electronic and Ionic Impact Phenomena*, Vol. II, Oxford University Press, London and New York (1969)

E. W. McDaniel, *Collision Phenomena in Ionized Gases*, Wiley, New York and London (1964)

D. Rapp and P. Englander-Golden, *J. Chem. Phys.* **43**, 5, 1464 (1965)

A. Rostagni, *Nuovo Cim.* **11**, 34 (1934)

A. Rostagni, *ibid.* **15**, 2 (1938)

B. L. Schram, F. J. de Heer, M. J. van der Wiel, and J. Kistemaker, *Physica* **31**, 94 (1965)

P. T. Smith, *Phys. Rev.* **36**, 1293 (1930)

R. F. Stebbings, B. R. Turner, and A. C. H. Smith, *J. Chem. Phys.* **38**, 2277 (1963)

G. L. Weissler, *Handbuch der Physik* **21**, 304, Springer, Berlin (1956)

W. Wien, *Handb. Exp. Phys.* **14**, Akad. Verlag Leipzig (1927)

I. P. Zapesochnyi and P. V. Feltsan, *Optics & Spectroscopy* **20**, 291 (1966)