# CHAPTER III

# FUNDAMENTAL KNOWLEDGE

## 3.1 Electron attachment reaction

When low-energy electrons collide with gas molecules, some of them are captured by the gas molecules, and negative ions are formed. This phenomenon is called "electron attachment" (Massay, 1976). Electron attachment depends on the electron energy, the structure of the gas molecule, and its electron affinity. There is a huge difference in the electron attachment probability of the gas molecules, and this high selectivity is reflected in the production of negative ions (Caledonia, 1975 and Massay, 1976, 1979). Therefore, electronegative impurities of very dilute concentration become negative ions by electron attachment, and they can be separated from the neutral gas (for example, $N_2$) in an electric field.

In the case of excessively high-energy electron colliding with a gas molecule, the molecule would not only be negatively ionized but may be dissociated or be positively ionized due to the loss of one electron from the molecule itself. In contrast, if an electron whose energy is too low reaches the molecular orbital, the electron can not be captured by the molecule. It is necessary to take into account the moderate (appropriate) range of electron energy when the attachment probability is to be enhanced. A great deal of effort has been devoted to generate or utilize electrons with a variety of energy range via quite a number of gas-discharge devices. However, the appropriate range of electron energy contributing exclusively to electron attachment generated by such devices has not been clarified because of the limitation of measurement devices and/or techniques.

At the exact moment when an electron is captured by a gas molecule, the molecule would be placed at the excited state. To become stable, the molecule must release the excess energy in quanta, for example, by collision with another electron, by collision with another gas molecule, by being decomposed, or by radiation. Various processes for the electron attachment reaction have been reported (Moruzzi and Phelps, 1966) as shown by Eqs. (3.1), (3.2), and (3.3). A mixture of an electron-attaching gas, AB, and an appropriate third body, M, is considered in these processes.

Dissociative attachment: $$e + AB \rightarrow A^- + B \quad (3.1)$$

Three-body attachment: $$e + AB + M \rightarrow AB^- + M \quad (3.2)$$

Radiative attachment: $$e + AB \rightarrow AB^- + h\nu \quad (3.3)$$

Since the electron attachment probability of the gas molecule is also dependent upon its electron affinity, it is reasonable to expect that a molecule that contains one or more atoms with high electron affinity would have high probability of electron attachment. For example, in a comparison between $SF_6$ and $N_2$, the electron affinities of S, F, and N are 200 kJ/mol, 333 kJ/mol, and -26 kJ/mol, respectively. So it is not surprising that the probability of electron attachment for $SF_6$ molecule is reportedly $10^{11}$ times that of $N_2$ molecule. This huge difference in the electron attachment probability among various kinds of gas molecules results in high selectivity in the formation of the corresponding negative ions. Therefore, a specific gas component whose concentration is extremely low can be separated from the main (neutral) gas in an electric field by utilizing the electron attachment reaction. Also one can expect the method based on electron attachment to be one of the most efficient methods of gas purification.

### 3.2 Principle of gas purification

**Figure 3.1** illustrates the principle of gas purification by removal of an impurity, AB, from an inert gas in a cylindrical corona-discharge reactor (Tamon et al., 1995). The corona discharge employed here is an efficient method to supply a sufficient amount of low-energy electrons to the gas stream. A wire stretched along the axis of the reactor acts as cathode and the outer cylinder acts as grounded anode. High voltage applied to the cathode induces corona discharge in the reactor. Electrons generated at the cathode drift to the anode along an electric field. During their drift, a portion of them collides with gas molecules. Negative ions, $A^-$, are thus selectively produced by electron attachment and they likewise drift to the anode as the electrons do.

In an ideal case, the number of electrons generated in the reactor is sufficient for all gaseous impurities to hitch up with electrons, and all negative ions completely deposit at the anode surface. In other words, the outlet gas is devoid of unwanted impurities and complete removal is achieved.

In reality, upon their arrival at the anode, certain kind of negative ions might not deposit on its surface. In this case such gaseous impurities can not be separated using the simple deposition-type reactor. It is therefore very important to capture most of the negative ions arriving at the anode surface. The idea of how to remove negative ions at the anode will be described later in **Section 3.3**.

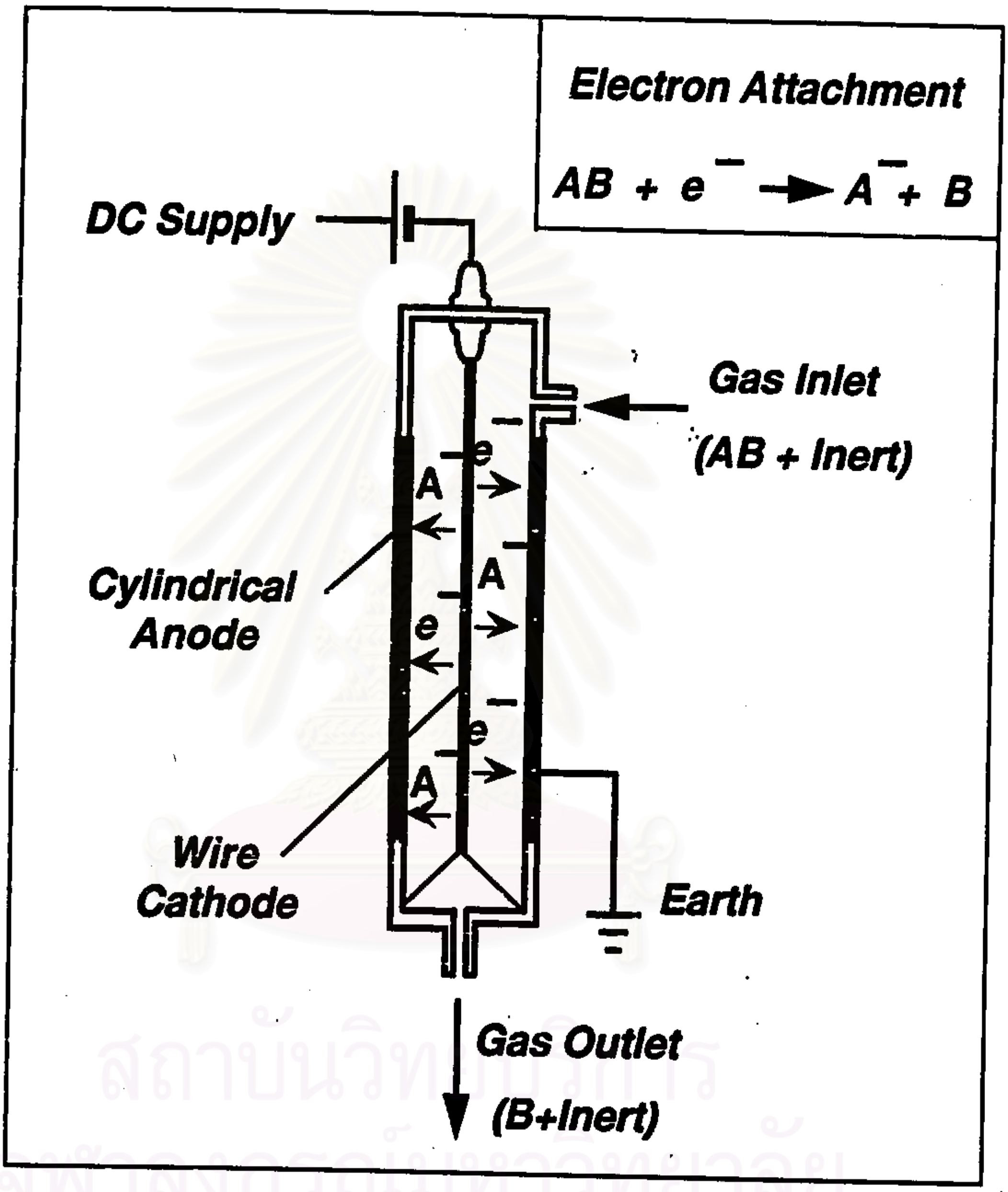


Figure 3.1 Principle of gas purification

Besides the above-mentioned removal mechanism associated with electron attachment reaction in a corona-discharge reactor, it is believed that other removal mechanisms may simultaneously affect the removal efficiency. When negative ions are produced in the reactor, they may possibly interact with other gas molecules via their electrostatic forces and negative-ion clusters may be formed. Each cluster then contains more than one of the gas molecules targeted for removal. When such clusters drift to the anode and deposit there, the removal efficiency is enhanced by the formation of negative-ion clusters.

Another possible mechanism contributing to the removal efficiency is the so-called radical reaction. When dissociative electron attachment also takes place in the reactor, not only negative ions but also reactive radicals are produced. In particular, radicals may readily be produced in the immediate vicinity of the cathode surface since high electric field strength exists there. It is logical to assume that removal efficiency would be enhanced by radical reaction.

The reaction of gas molecules with $O_3$ is frequently mentioned. Ozone reaction can take place when oxygen coexists in the gas stream. High energy electrons close to the cathode collide with $O_2$ molecules to dissociatively produce O radicals. O radicals can next react with $O_2$ molecules to produce $O_3$, which is reactive with various kinds of gases. Hence, ozone reaction is expected to contribute to the destruction of a number of gaseous impurities in the gas stream, thus improving the removal efficiency.

### 3.3 Types of reactor

As mentioned earlier, in some cases certain kind of negative ions produced by electron attachment may drift towards but not adhere easily to the anode surface. Thus they end up as electronegative impurities at the outlet of the simple deposition-type reactor, and cause a decrease in their removal efficiency. It is therefore essential to find out how to remove such negative ions at the anode. This motivated Tamon et al. to propose three types of reactor, as shown in **Figure 3.2**.

### 3.3.1 Deposition-type reactor

Some negative ions readily adhere to the anode surface of the reactor after releasing electrons there. Thus they may become solid particles or react with the metallic anode. The solid particles form a deposition layer on the anode surface. In this case, the so-called deposition-type (simple) reactor is adequate for the removal of negative ions. Periodical cleaning of the anode surface or its replacement is necessary to maintain high removal efficiency.

### 3.3.2 Sweep-out-type reactor

In some cases certain negative ions do not easily deposit on the anode surface but change back to the original molecules after releasing electrons at the anode surface. In such cases, the deposition-type reactor is not suitable because the original molecules of the gas impurities are not removed but diffuse back to the main gas stream. To solve this problem, the sweep-out-type reactor that uses a porous pipe made of sintered metal as anode is recommended. A small amount of the gas around the anode surface is swept out by suction through this pipe to restrict backward diffusion of the enriched electronegative impurities in order that the removal efficiency would be kept high. The swept-out stream with high concentration of the gas impurities can then be treated using a suitable conventional method.

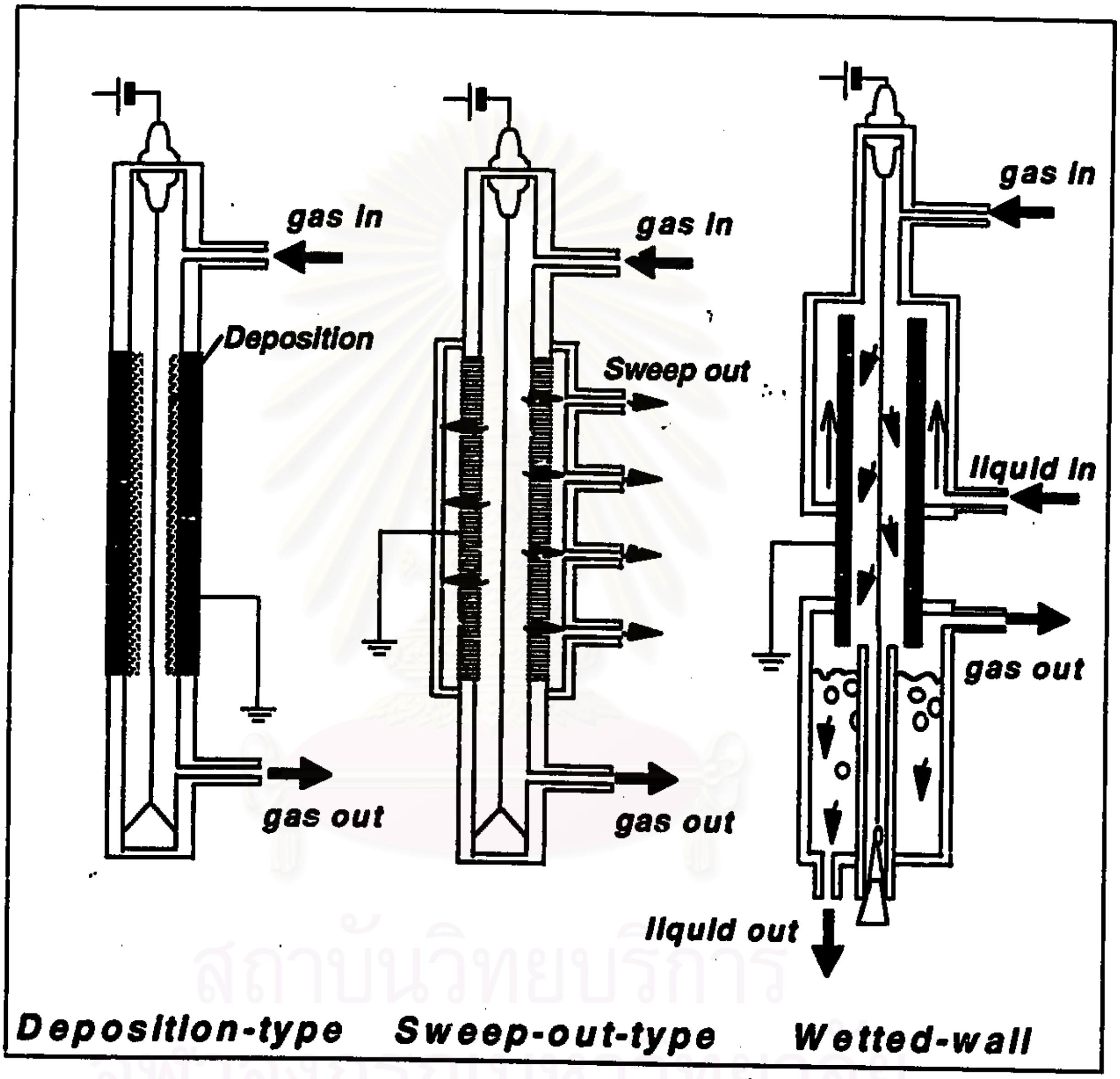


Figure 3.2 Concepts of corona-discharge reactor

### 3.3.3 Wetted-wall reactor

Another option to remove negative ions at the anode surface is the wetted-wall reactor. Negative ions reaching the anode of the reactor can be absorbed into a flowing liquid film on the anode surface. This absorption of the ions improves the removal efficiency. The advantage is the self-cleaning of the anode, which makes it suitable even for dirty gas streams containing dust and gaseous pollutants. The drawback is the need for a liquid (mostly water) treatment and recycle system.

Nevertheless, the prototype corona-discharge reactor to be constructed for this thesis is only the deposition-type one because it is easier to construct and operate, or more applicable as a first step of the fundamental study in a laboratory. The selected deposition-type reactor turns out to be satisfactory, as described later.