

APPLIED ATOMIC COLLISION PHYSICS

*Editors: H. S. W. MASSEY, E. W. McDANIEL,
and B. BEDERSON*

Volume 5

Special Topics

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Treatise Preface

Research in atomic physics and especially in the physics of atomic collisions has developed at an explosive rate since the Second World War. The high rate of increase of knowledge of atomic collision processes has been of great value in many applications to pure and applied physics and chemistry. For the full understanding of the physics of planetary and stellar atmospheres, including those of the earth and the sun, detailed knowledge is required of the rates of a great variety of atomic and molecular reactions. Gas lasers depend for their operation on atomic collision processes of many kinds, and a knowledge of the corresponding reaction rates is important for laser design. The release of energy by controlled nuclear fusion offers a possibility of an effectively infinite source of power in the future. Many aspects of the complex techniques involved are affected by atomic reactions. Again there are many applications of collision physics to the study of condensed matter.

These major activities have expanded rapidly at a rate which has been accelerated by the availability of data and understanding from atomic collision physics. There are many smaller areas which depend on this subject.

In these five volumes we planned to give an account of the wide range of applications which are now being made, as well as the additional requirements for further application. Volume 1 deals with applications to atmospheric and astrophysics, Volume 2 to controlled fusion, Volume 3 to laser physics, and Volume 4 to condensed matter. Volume 5 includes various special applications.

In all cases the emphasis is on the discussion of these applications and the atomic physics involved therein. However, sufficient background is provided to make clear what has been achieved and what remains to be done through further research in collision physics.

We are much indebted to Academic Press for the ready assistance they have afforded us at all times.

H. S. W. MASSEY
E. W. MCDANIEL
B. BEDERSON

Preface

The first four volumes of "Applied Atomic Collision Physics" each deal with a different major field of application, one which is the subject of intense activity in research and/or development. Volume 1 is concerned with atmospheric physics and astrophysics, Volume 2 with controlled fusion, Volume 3 with gas lasers, and Volume 4 with condensed matter (especially surfaces). There remain many other areas of application that should be treated, and in this final volume we have grouped a number of additional topics from various fields and given them what we believe is at least minimal coverage. Some of the applications treated in this volume deserve one or more entire books for their coverage, but it is hoped that this volume, when combined with the other four, will provide the reader with a good perspective of the applications of atomic collisions.

E. W. MCDANIEL

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1

Ultrasensitive Chemical Detectors

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I. Introduction

In the first half of this century, the investigation of ionization phenomena in gases was a major interest of physicists. It led naturally to the quest for knowledge about atomic and subatomic phenomena, until eventually the interest in gaseous ionization itself became like one of those once bustling, now abandoned, weed-choked waterways, waiting only a reawakening as an area where more leisurely interests can be enjoyed.

At the time when gaseous ionization phenomena were closely studied, the disciplines of science were more isolated from one another than now. As a result, the immense fund of knowledge gathered was rarely available to chemists or engineers in spite of its great potential value to them. In a like way, the experience of chemists knowledgeable in the handling of gases and of keeping them pure was not often passed on to experimenters in gaseous ionization. As a consequence, the literature of the period is peppered with papers that misinterpreted as physical phenomena effects that, with hindsight, are now known to be the consequence of trace impurities in the gases used.

In the relative isolation of the physics laboratory, the experimenter was sometimes unaware of the ubiquitous distribution of intensely electron-attaching vapors, such as, for example, that of carbon tetrachloride, which in those days was a common cleaning solvent and fire extinguisher. It was not well known that the unintended presence of as little as 1 part in 10^9 of this and similar vapors would be sufficient to invalidate some experimental measurements completely.

In 1952, James and Martin put into use the gas chromatograph. This most powerful of analytical techniques was enthusiastically pressed into service in nearly every branch of chemistry, and it was not long before there were demands for even greater sensitivities so that its use could be extended still further. The original detector developed by Martin and James (1956), the gas density balance, although near ideal and universal in operation, could not detect vapor concentrations much below 1 ppm by volume. Martin recognized the need for greater sensitivities and asked me, as one with a nodding familiarity with atomic collision processes, if it would be feasible to develop ionization detectors for gas chromatography. In such a climate, it was not long before those of us concerned with the need to invent new detectors became aware of the mountain of knowledge which had accumulated. It was not difficult to extract its riches. All that we needed were atomic or molecular collision processes that could be exploited to develop new and sensitive methods able to transduce an electrical signal from the evanescent vapor concentrations emerging in the effluent stream of a gas chromatograph column.

Although gas chromatography and vapor detectors dominate the use of atomic collision processes, in chemical analysis there are other important applications, especially mass spectrometry. Indeed, in some senses, the mass spectrometer is the most highly evolved of all gas and vapor detectors. Mass spectrometry, however, will not be discussed in this chapter, partly because the topic has been extensively covered elsewhere in this treatise, whereas the simple atomic collision detectors have not, but also because the simple ultrasensitive detectors form a coherent group and are a topic worthy of independent discussion.

The practical application of atomic devices for chemical detection is widespread. In a substantial proportion of offices and factories there are ionization fire detectors, and, in response to a more recent need, at most airports explosive vapor detectors are to be seen.

Ultrasensitive ionization methods are often used to observe mass transfer in gases and liquids through the use of inert tracers. Research in fields ranging from meteorology to medicine has benefited from this application of their exquisite sensitivity. Just as important is their application in engineering for the detection of leaks. So great has been the demand for sensitive detectors that they have developed as inventions with often little or no attempt to understand in detail the physical basis of their operation. To the working chemist or engineer, they represent a way of solving a problem and, given a physical phenomenon with which some property of a known and of an unknown sample could be compared, that is all that is needed.

The atomic collision processes forming the basis of these inventions are often sufficiently well understood to allow the development of absolute methods of measurement, but there is rarely the time or the inclination to do this.

It will require a great deal more research and analysis and the writing of a lengthy book to cover this topic of chemistry adequately; in the meantime this chapter may provide the synopsis.

II. Common Factors

Certain properties and requirements are shared in common by all of the detectors of this group, and it is helpful first of all to consider these before passing on to a detailed description of each specific detector.

Table I lists the ultrasensitive gas and vapor detectors now rendered practicable and in widespread use. Of these, only the Penning effect detectors (Penning, 1934), which exploit the ionizing collisions between excited rare gas atoms and other molecules, can be truly considered as atomic collision devices. The others depend for their operation on collisions between molecules or with fundamental particles like electrons and photons. It would be

TABLE I
Detector Characteristics

Detector and reaction	Abbreviated title	Energy level (eV)	Detectivity		Ionization and quantum yield	Linear range
			Molecules per second	Least detectable concentration		
Electron capture	ECD	0.025–0.040	10^6	10^{-13}	0.3–1.0	10^4
Flame ionization	FID	~2.0	10^9	10^{-10}	10^{-5}	3×10^5
Photoionization	PID	9–21	10^8	10^{-11}	10^{-3}	10^5
Penning effect	PED	11.57–21	10^8	10^{-11}	10^{-3}	10^4
Chemiluminescent	CLD	~2.0	10^{10}	10^{-8}	10^{-7}	10^3
Flame photometric	FPD	~2.0	10^{11}	10^{-8}	10^{-7}	10^3

arbitrary to limit our discussion to Penning effect detectors on this account only, since the list comprises a very comparable group of devices. They all are used interchangeably as gas chromatography detectors.

Table I also lists the reactions exploited in the detectors and compares their performances and lists the abbreviated title of each detector, which will be used henceforth in the text. The detectors in the table are the survivors of a vigorous evolutionary struggle during the past twenty years. Some, like the PID and the PED, hang on precariously in specialized niches, while others, such as those which exploited glow discharge and similar plasma phenomena for detection, have become extinct.

Whatever the reaction or process, the successful detectors are seen to operate at low or very low energy levels in physical terms. Obviously, this is the energy range of chemical reactions: from thermal (0.025 eV) to about 10 eV. However, there is another, more important reason for the success of low energy devices, which arises directly from their principal use as gas chromatography detectors. The ideal gas chromatography detector is one in which the chosen carrier gas is completely transparent and yet in which each molecule of the substance sought can be seen.

For the benefit of those readers unfamiliar with the gas chromatograph, it is briefly described as follows: A mixture of gases or of volatile compounds to be analyzed is introduced as a vapor concentration pulse into a flowing stream of some inert carrier gas. The pulse is immediately passed into a long tube, which may be either empty or filled with uniform-sized grains of powder. The inner walls of the tube, or the powder, are coated with a non-volatile solvent or solid adsorbant, whose function is to dissolve or adsorb the components of the mixture. In general, the more volatile and less polar

compounds adsorb or dissolve least: consequently, they move faster through the column and eventually are completely separated from one another. Often the components emerge as pure compounds: indeed, such is the resolving power of the method that compounds differing only in their isotopic composition can be separated in a single pass.

The gas chromatograph functions best at near to ideal gas conditions. Consequently, the preferred carrier gases are the permanent gases helium, argon, nitrogen, and hydrogen. In addition the vapors, with their less than ideal gas properties, are most efficiently separated when dilute.

All four of the common carrier gases have ionization potentials greater than 15 eV and with one exception, hydrogen, which is less often used, are chemically inert. They provide the inert background against which the more reactive vapors are recognized. It was the properties of these gases which set the environment in which the successful detectors evolved. Furthermore, all of them use the gas phase as the reaction medium. The solid part of the detector structure is only for containment, for isolation, and for gaseous and electrical conduction. Early in the development of detectors, some sensitive devices were invented that depended on phenomena taking place at solid surfaces, for example, the change in work function of a metal electrode following the adsorption of vapor. It was soon found that these behaved erratically and were irreproducible in their responses. In spite of their simplicity and great sensitivity, they were soon abandoned in favor of those listed in Table I.

This chapter is concerned with ultrasensitive devices, so it is useful to consider the factors which set the lower limit of detection, for this also is a feature shared in common.

In principle it should be possible, especially with a very inert carrier gas such as helium, to ionize or to cause photon emission from a single molecule. In practice, this has been achieved with the ionization of cesium vapor by laser radiation. This can be considered a special example of the photonization detector.

Although it is a stimulus to know that such extremes of detectivity are not beyond reach, in practice, the degree of contrast is never so great as between cesium atoms and a helium background; the limit of detection is set by the electron capture (ECD) at about 3×10^5 molecules⁻¹. The difference between the ultimate and the realizable comes mostly from the presence of a background of ionization, from impurities in the carrier gas stream, or from the process of ionization itself. This background is normally greater than 10^7 ion pairs or photons per second.

The ease with which polyatomic solute molecules are distinguished from simple inert carrier gas atoms is one reason that gas chromatography and ionization detectors developed symbiotically; but another and equally