but these are refinements which would take us beyond the field of our discussion.

8-9. Experiments on Excitation Potentials.—In the preceding sections we have investigated the ability of an atom to absorb energy in the form of radiation, and we have seen that the energy so absorbed is taken up selectively, the atom being raised from the normal to an excited state. Furthermore these radiative energy interchanges are observed to occur in such a way that the postulates made in regard to emission spectra, particularly with reference to the selection rules governing transitions accompanied by the emission or absorption of radiation, are entirely confirmed. In the present section we shall investigate the ability of an atom to absorb energy supplied in the form of the kinetic energy of a bombarding electron. On the basis of the previous sections we should anticipate that the kinetic energy of an electron is also absorbed selectively in amounts corresponding to the energies of the various stationary states above the normal level of the atom. However, the selection rules we have used in the past may lose their validity, as the mechanism, whatever it is, for the absorption of a photon may be entirely different from that for the absorption of the kinetic energy of an electron. If the values of the energy levels found with electron bombardment compare favorably with those deduced spectroscopically, we are afforded the most direct and convincing evidence that the stationary state concept is correct. Exact agreement cannot be expected, since an error of 0.1 volt corresponds to 810 wave numbers.

There are a number of experimental methods by which the problem may be attacked. We may focus our attention on the electrons and measure their residual energy after they have been accelerated by an electric field through a region containing atoms of the gas or vapor. If the atoms are capable of absorbing energy only in the characteristic amounts indicated by our previous theory, the collisions will be perfectly elastic (no energy will be lost by the electrons), until the electrons have progressed far enough through the field so that their energy is equal to, or slightly greater than, the lowest of these critical amounts. Then, at a collision, this kinetic energy may be lost to an atomic system raising it to the lowest excited state; as a first approximation the electrons will be brought to rest. If they are still in an electric field after the collision, they may gain more energy and repeat the process. If an inelastic collision does not occur as soon as an electron acquires sufficient energy, it may gain enough more to excite a higher state of the atom. Thus, as the potential difference between the electrodes is increased, the residual energy of the electrons should pass through maximum and minimum values, the maximum values occurring just before one of these characteristic energy losses. This residual energy of the electrons is measured by means of a retarding potential against which they must be able to travel in order to be recorded by a galvanometer. As an alternative method of observing these critical energy losses, the radiation emitted by the atoms which have been raised to excited states at inelastic collisions may be detected by either photoelectric or spectroscopic means. This technique, however, is more difficult. Finally, for the measurement of the series limit, *i.e.*, the energy necessary to remove completely an electron from an atom, we may investigate the particular electron speeds at which positive ions are formed in the gas.

The original so-called partial-current method of Franck and Hertz[1] is a simple and effective way of examining the changes in the residual electron energies as the total potential difference is varied through which the electrons fall in passing through a gas or vapor. It is suitable for inert gases and metallic vapors since these have no appreciable electron affinity, *i.e.*, there is no tendency for an electron to become attached to an atomic system, resulting in a negative ion. It is particularly appropriate for use with high pressures. In this method, electrons from a filament are accelerated by a variable potential V_a toward a grid, and, if they have lost no energy at the impacts occurring between these electrodes, they are capable of advancing further against a very small retarding field V_r between this grid and a collecting plate. The electrons reaching the plate are recorded by a galvanometer. As the accelerating potential V_a is increased from a small value, the electron current to the plate also rises. In this region, elastic collisions with the gas atoms occur and the original direction of motion of an electron is altered, but eventually almost all of the electrons reach the plate. When, however, V_a is equal to, or slightly greater than, the minimum excitation potential of the gas, some of the electrons collide inelastically, and the energy which they possess after exciting an atom is insufficient to allow them to proceed against the retarding field V_r, and the galvanometer current drops off. The current does not decrease abruptly, for, as the potential difference is increased, the inelastic collisions are able to occur nearer the filament and many of the electrons are able to gain sufficient energy after the collision to surmount the potential barrier V_r and to reach the collecting plate. Also, as we have seen, the electrons are emitted from the filament with a distribution of velocities which tends to smooth out any sharp discontinuities in the curve. As the potential difference is increased, the electrons gain sufficient energy again to excite the lowest level of another atom and a second decrease in galvanometer current is observed.

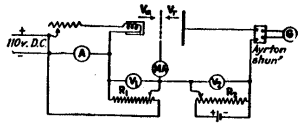

FIG. 8-9.—A diagrammatic sketch of the Franck and Hertz partial-current method of detecting inelastic impacts of electrons with gas atoms.

[1] FRANCK and HERTZ, *Verh. Deut. Physik. Ges.*, **16**, 10 (1914).

We thus expect a series of maxima and minima in the galvanometer current, corresponding to single and multiple inelastic collisions, as the accelerating potential is increased. A high concentration of atoms in the space traversed by the electrons favors the occurrence of inelastic collisions at which the lower excited states are produced, for the free paths between collisions are shorter and there is a correspondingly smaller chance that an electron can gain sufficient energy between inelastic collisions to excite the higher states. The investigation of such higher levels is more feasible at small gas pressures and with a more refined type of apparatus.

Quite acceptable determinations of the lower energy levels of the mercury atom can be made with a General Electric thyratron. This is a vacuum tube containing a small amount of mercury; the small three-electrode type such as the FG-27 is suitable for this experiment. The density of the mercury vapor in the region surrounding the electrodes can be controlled by placing the tube in a small electric oven. Such an oven can be made conveniently of heavy asbestos board with about 10 ft. of nichrome heating wire in the form of a $\frac{1}{2}$-in. helix fastened around the inside of the walls. A mercury thermometer or calibrated thermocouple capable of covering the range from room temperature to about 250° C. may be used to measure the temperature. The electrical connections are shown in Fig. 8-9. If direct current is available, the same supply may be used for the filament and for the accelerating potential, as shown in the diagram. Otherwise a step-down transformer may be used for heating the filament and small-capacity dry cells for the accelerating potential V_a. This potential is controlled by the potentiometer R_1 and measured with the voltmeter V_1, which should be read to 0.1 volt. The milliammeter in the grid circuit is not essential. The small constant retarding potential V_r is supplied by the battery and potentiometer R_2. This potential, as measured by V_2, may be conveniently chosen at about 0.5 volt; the value is not critical. The galvanometer should be of moderate sensitivity; one giving a deflection of 2,000 mm. at a meter per microampere is adequate.

Figure 8-10 indicates typical results obtained with an FG-27 thyratron maintained at 210° C. The vapor pressure at this temperature is about 24 mm. Hg, and the density of the atoms is so great that only the lowest excited state is ever produced. The presence of a contact potential between the filament and grid vitiates the absolute readings of the voltmeter; however, differences between these readings eliminate the unknown error and it is seen that the average potential between peaks is 4.85 volts. This agrees almost exactly with the energy differences, as found spectroscopically, between the lowest level $6s^2\ {}^1S_0$ and the first non-metastable excited term $6s6p\ {}^3P_1$. The transition between these levels

gives rise to the resonance line 2536.52 Å or 39,412.9 wave numbers which corresponds to 4.86 electron volts.

A slightly more complicated apparatus, also due to Franck and Hertz,[1] which contains an additional grid, is capable of higher resolving power and indicates many additional peaks corresponding to the values of other energy levels measured from the normal state when used at low gas

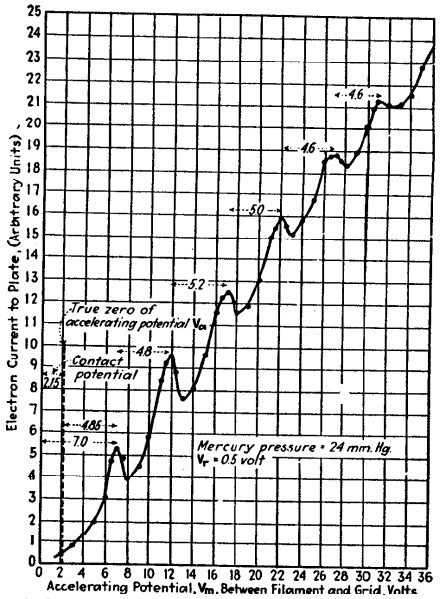

FIG. 8-10.—An inelastic impact curve obtained with an FG-27 thyratron, showing the lowest critical potential of mercury, at 4.86 volts. The circuit used was that of Fig. 8-9.

pressures. Several of these critical potentials represent kinetic energy transfers for which the equivalent transition accompanied by radiation is not permitted. This shows that, although the atom can absorb kinetic energy only in the same discrete quantized amounts in which it can absorb radiation, nevertheless the selection rules applicable to the latter process do not apply at these kinetic energy transfers. Certain of these additional peaks can be observed with a thyratron with the mercury vapor pressure adjusted to about 0 mm., but the difficulty of observing

[1] Franck and Hertz, Physik. Zeits. 17, 409 (1916).

these maxima with a tube not designed for the purpose prevents satisfactory results. An ordinary screen-grid radio tube which has been opened to admit a few drops of mercury and then reevacuated, has the advantage of an extra control grid. The accelerating potential V_a is applied between the filament and the first grid, then a very small field (0.1 volt) continues to draw the electrons toward the second grid, between which and the plate the retarding potential V_r is applied. This arrangement has the advantage that there is a large, approximately field-free region between the grids in which electrons with the energy corresponding to V_a may collide; this greatly increases the resolving power of the apparatus. However, the grid spacings in an ordinary commercial tube are not the most favorable for this purpose, and as a consequence the curves of Franck and Hertz cannot be reproduced in detail. In endeavoring to measure these higher critical potentials it is a fundamental necessity that the temperatures of the tube and filament should be kept very constant; otherwise the slight variations in temperature, which greatly alter the recorded plate current, completely mask the small peaks.

A still more sensitive method, which may be used with a special tube, has also been devised by Hertz.[1] This method, which is indicated in Fig. 8-11, is capable of great precision and, furthermore, avoids the superposition of peaks that limits the sensitivity of the methods which have been previously described. Electrons from a filament are accelerated by a variable potential V_a through an opening into a field-free region where they collide with atoms of the gas or vapor. If the impacts are elastic, some of the electrons are deflected without loss of energy out through the sides of the gauze cylinder defining the field-free region and are able to advance against a retarding potential V_r of 0.1 volt between the gauze and a surrounding plate. As the accelerating potential V_a is increased in small steps, the current to the plate, as measured by a galvanometer, is observed both with $V_r = 0.1$ and $V_r = 0$; as long as the collisions are elastic the two galvanometer readings are approximately the same. When the potential is reached at which inelastic collisions first occur, the electrons lose practically all of their energy and retain an insufficient amount to reach the plate when the retarding potential of 0.1 volt is applied. Hence, at this potential, the galvanometer readings for the two values of V_r are found to differ, and this difference gives a measure of the number of electrons emerging from the gauze with energies less than 0.1 volt, *i.e.*, the number which have suffered inelastic collisions. Since the collisions occur in a field-free region, there is no possibility of an electron regaining energy from the field after an impact as in the original method, and repetitions of the same critical energy loss do not occur. Hence the contact potential may not be determined directly, but it may be inferred if one of the critical

[1] HERTZ, *Zeits. Physik*, **18**, 307 (1923).

potentials is known or if a mixture of two gases is used for one of which the critical potentials are known.

It is also possible to obtain further confirmatory evidence of stationary energy states by observing the optical effects produced by the excited atoms which are formed at these inelastic collisions. Every time an atom is excited by a collision with an electron it is in a position to return to its normal state by the emission of radiation, if the excited state is not metastable. This radiation may be detected by some suitable means. It has been observed photoelectrically by Franck and Einsporn,[1]

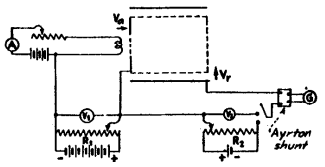

FIG. 8-11.—The Hertz method of detecting inelastic impacts of electrons with gas atoms.

using a tube similar to that described above containing two grids and a plate. The radiation emitted when an excited atom returns to its normal level falls on the plate and liberates a photoelectron; this photoelectric current from the plate is recorded by an electrometer. The radiation emerging from the region containing the excited atoms has also been observed directly by means of a spectrograph. Such observations have been made by a number of investigators, notably by Foote, Meggers, and Mohler[2] who have shown that one, two, three, and more spectral lines are produced as the energy of the bombarding electrons is successively increased through the values of the various excited states. As the technique is rather difficult and the necessary exposures very long, the detailed experimental procedure will not be given.

8-10. Experiments on Ionization Potentials.—The determination of the critical electron energy necessary for the complete removal of an electron from an atomic system may also be made with the type of apparatus which has already been described. The simplest arrangement for measuring this ionizing potential in the case of mercury vapor is by the use of the thyratron which was previously employed for the measurement of the critical excitation potentials. It is merely necessary to transfer the plate lead in Fig. 8-9 from the grid to the filament, *i.e.*, connect the positive terminal of V_2 to the negative rather than the positive terminal of V_1. This maintains the plate 0.5 volt negative with respect to the filament for all values of the grid potential, thus preventing any electrons emitted by the filament from reaching the plate. Any

[1] FRANCK and EINSPORN, *Zeits. Physik*, **2**, 18 (1920).

[2] FOOTE, MEGGERS, and MOHLER, *Phil. Mag.*, **42**, 1002 (1921).

positive ions formed in the region between the grid and plate are drawn to the latter electrode and are recorded by the galvanometer. For this observation the temperature of the furnace should be reduced till the vapor pressure of the mercury is about 0.5 mm. The galvanometer remains undeflected as the accelerating potential V_a of the electrons is increased until the ionizing potential is reached. At this point a few ions are formed near the grid, some of these are drawn to the plate, and the galvanometer is deflected in the direction indicating the reception of positive charges. The potential at which this occurs, as given by the voltmeter V_1, must be corrected for the contact potential between the electrodes as determined by the critical-potential measurements in order to obtain the true ionizing potential. This is found to be 10.4 volts which is in excellent agreement with the energy difference between the ground state $6s^2\ {}^1S_0$, and the ion as determined spectroscopically, which is 84,178.5 wave numbers or 10.39 electron volts.

An alternative and extremely delicate method for detecting ionization potentials has been devised by Hertz.[1] Electrons from a filament F_1 are accelerated by a variable potential V_a into a field-free box where they collide with the atoms or molecules of the gas. The box contains a filament F_2 between which and the walls an accelerating potential V_b is applied. This potential is considerably less than the ionizing potential of the gas, and the filament is so hot that the current from it to the box is limited by space charge. As long as V_a is low enough so that the electrons from F_1 do not produce any ions in the box, the space-charge limited current as measured by a galvanometer remains constant, but when V_a is increased to such an extent that ions are formed, these neutralize some of the space charge around F_2 and the current through the galvanometer increases. The method does not permit any direct determination of the contact potentials between the electrodes, but by using two gases, for one of which the ionization potential is known, this additive constant may be determined.

A tube suitable for the measurement of both the excitation and ionization potentials by the Hertz methods is shown in Fig. 8-12. The electrical circuit in the figure is that for the measurement of ionization potentials; the circuit for excitation-potential measurements is given in Fig. 8-11; the second filament F_2 is connected to the gauze cylinder in the latter case. The two filaments pass through the presses on tungsten leads, nickel rods of suitable length are welded to these, and the filaments spot-welded across the ends. F_1 should be a coated platinum strip with a V-shaped notch in the center, in order to provide an approximately equipotential source; F_2 is an ordinary hairpin type filament of about 5-mil tungsten. The outer collecting cylinder fits snugly in the main part of the tube and the inner cylinder of nickel gauze is separated from it by two rings

of Pyrex cane. These two electrodes are inserted before the filaments are sealed into place. The end of the gauze cylinder facing the filament F_1 is a nickel disk containing a gauze-covered opening immediately opposite the filament. The space between this opening and F_1 should be as small as possible, *i.e.*, of the order of 1 to 2 mm. The electrical connection to the inner cylinder may be made with a fine flexible helix of nickel wire spotted to a light tungsten rod for sealing through the wall; the sealing in is done after the electrode is in place. The connection

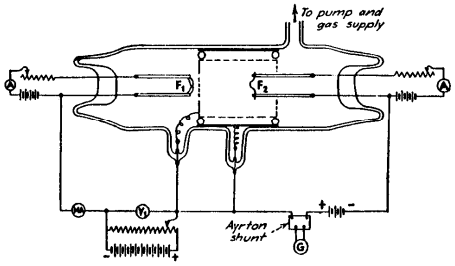

FIG. 8-12.—A diagram of an apparatus for the Hertz method of detecting ionization potentials of a gas. The tube indicated is also suitable for use with the circuit of Fig. 8-11 for measuring radiation potentials. For ionization-potential measurements the cylindrical grid and plate are connected together to act as a single electrode.

to the outer cylinder can be made by a spring spotted to a tungsten wire sealed through the wall which presses against the outer surface of the cylinder. When the electrodes are all in place, the apparatus is sealed to a vacuum system and baked out at about 400°C. for several hours; during the process the filaments should be heated a little above the temperatures at which they are to be used. The tube is then ready for operation and the gas to be used is admitted at a pressure of a few millimeters of mercury. The optimum pressure depends on the gas and the exact electrode separations, and hence it must be found by trial. The types of curves obtained using the circuits of Figs. 8-11 and 8-12 are shown in Fig. 8-13 for neon. The abscissas are the voltages V_a (corrected for contact potentials), and the ordinates are the differences between the galvanometer currents for curve A, the peaks of which represent excitation potentials, and the current from the filament F_2 for curve B, the break in which indicates the ionization potential. As the contact potential between F_2 and the outer cylinder is not zero the abscissas of both curves must be corrected separately with a gas such as argon for which the excitation and ionization potentials are accurately known.

It should also be mentioned that the apparatus described in Chap. IV for the measurement of e/M for positive ions may be used for the measure-