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Some Factors Affecting Action Cross Section for Collisions of the Second Kind between Atoms and Ions

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Enhancement of spark lines of Ag, Au, Al and Cu in neon and helium arcs.—Experiments are described in which the relative probability of the excitation of terms in the spark spectra of metals by impacts of the second kind with ions of helium and neon was determined as a function of the resonance discrepancy. The enhancement of certain levels excited by collisions of the second kind relative to their excitation in a condensed spark or an arc was taken as a measure of the probability of the excitation in a collision of the second kind. The results show a definite resonance effect but sufficient data have not yet been obtained to determine with certainty an empirical formula. The experiments show that, besides resonance discrepancy, the type of level being excited is an important factor in determining the probability of excitation. For excitation by helium and neon ions, triplet levels are strongly preferred over singlet levels in the case of several metals investigated. This preference is not that sort which is predicted by the Wigner rule.

I. Introduction

The term "collision of the second kind" was introduced in 1921 by Klein and Rosseland.[1] They showed from a consideration of thermal equilibrium that if ionizing and exciting collisions of electrons with atoms were possible, the reverse collision, in which the excitation energy of the atom was given to the electron in the form of kinetic energy, must also be possible. This idea was extended by Franck[2] and his coworkers, who showed that collisions also occurred between excited and unexcited atoms in which the excitation energy was transferred from one to the other. These are also included in the term "collisions of the second kind." Thus we may define a collision of the second kind as a collision between an excited or ionized atom or molecule and a second particle, in which the energy of excitation or ionization of the first particle is transferred to the second particle.

On the basis of this definition we may classify collisions of the second kind as follows: (1) Collisions between excited atoms and electrons, in which the excitation energy goes into kinetic energy of the electron. (2) Collisions between excited atoms and normal atoms, in which the excitation energy is transferred from one atom to the other, the difference going into kinetic energy. (3) Collisions between excited atoms and normal atoms, in which the second atom is ionized, or ionized and excited, while the first returns to normal. This leaves a free electron after the collision. (4) Collisions between ions and normal atoms, in which the ion returns to a normal atom and the normal atom is ionized or ionized and excited. This involves the transference of an electron as well as energy.

In every case where the word atom is used above, "atom or molecule" is to be understood. In general, the states of excitation before and after a collision will not involve exactly the same amounts of energy. The difference, called the energy discrepancy, will come from, or go into, kinetic energy of the colliding particles.

The present paper deals only with the fourth of the above classes. The ions used were helium or neon ions, and the normal atoms were metals. In every case, the metallic atom was ionized, and its spark spectrum excited. An attempt has been made to determine the relation between energy discrepancy and the probability of excitation of a given level, as well as the importance of other factors affecting the probability.

Theoretical consideration has been given this problem by a number of authors.[3] The theo-

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[1] Klein und Rosseland, Zeits. f. Physik 4, 46 (1921).

[2] Franck, Zeits. f. Physik 9, 259 (1922). Cario and Franck, Zeits. f. Physik 17, 202 (1923).

[3] Kallman und London, Zeits. f. physik. Chem. 2B, 220 (1929). Morse and Stueckelberg, Ann. d. Physik 9, 579 (1931). Frenkel, Zeits. f. Physik 58, 794 (1929). Rice, Proc. Nat. Acad. Sci. 17, 34 (1931); Phys. Rev. 38, 1934 (1931). Landau, Zeits. Sow. 1, 88 (1932). London, Zeits. f. Physik 74, 143 (1932).

retical results are expressed in terms of an action cross section which is defined by the equation: $q=2\pi\int_0^\infty r\cdot p(r)\cdot dr$, where q is the action cross section, r the distance of closest approach of the two particles, $p(r)$ the probability that the transfer of energy will take place when the particles approach to that distance.

Most of the theoretical investigations have been concerned with the relation between energy discrepancy and the probability of collision. Thus, Kallmann and London find that the action cross section is proportional to $1/\sigma^{2/3}$ where σ is the energy discrepancy. This treatment was applied to the second class of collisions listed, and did not include the effect of the kinetic energy of the colliding particles, although the authors pointed out the importance of this factor. Morse and Stueckelberg included the kinetic energy in their treatment and arrived at a more complicated expression.

Wigner[4] has shown from symmetry considerations that certain types of levels may be preferred over others. His considerations apply particularly to collisions of the second type listed above. They do not apply to those considered in the present paper.

II. Experimental Method

The experimental method has consisted in comparing the intensities of lines representing transitions from spark levels when these levels were excited by collisions of the second kind, with the intensities of the same levels excited by electronic collisions. The method of excitation by collisions of the second kind was that used by Duffendack and Black.[5] The metal whose spectrum was to be examined was placed inside a tungsten resistance furnace in a tungsten trough. The furnace consisted of a tube of tungsten sheet about 2 cm in diameter and 9 cm long. A tungsten filament ran along the axis of this tube, and a low-voltage arc was run from the filament to the walls of the furnace. The whole furnace was enclosed in a vacuum tight case into which the rare gas, whose ions provided the excitation, could be introduced at the desired pressure. The low-voltage arc was thus run in a mixture of rare gas and metallic vapor. It was found that the spark spectra of the metals used were not excited in this type of discharge when the pure metal vapor was used, so it was considered safe to assume that the excitation of the higher spark levels was entirely due to collisions of the second kind.

A condensed spark in air between electrodes of the metal being investigated was used as a "normal" source. The field in the spark is high and thus the electronic energies should be far enough above the levels to be excited to give a "normal" distribution. In the case of copper it was found that the relative intensities of all the lines coming from a group of levels situated within a quarter of a volt of each other had the same intensity, within the errors of measurement, in the spectrum of an arc in air as they had in the condensed spark in either air or hydrogen. The relative intensities of lines coming from more widely separated levels was quite different, however. Since the levels excited by collisions of the second kind lie quite close together, the relative intensity of the lines coming from them probably would not be much affected by the spark voltage. The method of measuring intensities was that described by Thomson and Duffendack.[6]

III. Experimental Results

The first excitation studied was that of the copper spark spectrum by neon ions, which has been previously reported by Duffendack and Black[5] and by Frerichs.[7] The copper spark spectrum has four levels whose energies (measured from the normal atom) lie just below the neon ionization potential. The differences between these energies and the neon ionization energy is given in Table I under the heading "energy discrepancy." The table contains a list of lines from these levels, with their relative intensities in the low-voltage arc in neon, and in the arc or spark in air. The ratio of these intensities is given as "enhancement." The intensity of the 2544.96 line was arbitrarily given the same value in the two discharges.

Fig. 1 shows, graphically, the relation between

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[4] Wigner, Nachr. Götting. Ges., p. 375, 1927.

[5] Duffendack and Black, Phys. Rev. **34**, 35 (1929).

[6] Thomson and Duffendack, Phys. Rev. **40**, 1042 (1932); J. Op. Soc. Am. (In print.)

[7] Frerichs, Ann. d. Physik **85**, 362 (1928).

TABLE I. *Copper spark lines enhanced in the neon arc.*

Line	Initial level	Normal intensity	Intensity in neon	Enhancement	Energy discrepancy (volts)
2526.73	$(d^9s)^3D_3$	2.2	2.2	1.0	0.40
2544.96		10.0	10.0	1.0	
2689.46		4.7	4.7	1.0	
Average				1.0	
2506.41	$(d^9s)^3D_2$	6.9	19.7	2.8	0.36
2598.96		2.8	7.4	2.6	
2666.44		1.8	4.4	2.4	
2713.66		4.7	13.3	2.8	
Average				2.7	
2485.95	$(d^9s)^3D_1$	4.3	57	13.2	0.16
2590.68		2.1	32	15.2	
2703.34		3.8	57	15.0	
2721.84		1.9	27	14.7	
Average				14.6	
2529.48	$(d^9s)^1D_2$	4.2	40	9.5	0.12
2600.43		4.4	44	10.0	
2701.12		4.8	48	10.0	
2718.96		3.8	35	9.2	
Average				9.7	

the enhancement of the d^9s levels of the copper ion and the energy discrepancy for excitation by neon ions. It will be noted that the points for the triplet levels lie on a smooth curve. But the point for the singlet level does not fall on this curve. Despite the fact that the energy discrepancy for this level is less than for any of the triplet levels, its enhancement is less than that of the $^3D_1$ level. If the enhancement of the singlet level had been consistent with that of the triplet levels, it would have had an enhancement of about 18.5 instead of 9.7. Thus, there seems to have been a definite preference for the triplet levels in the collisions between neon ions and copper atoms. Similar preferences were exhibited in the excitation of levels in the spark spectra of gold and aluminum by helium and neon ions and will be discussed later.

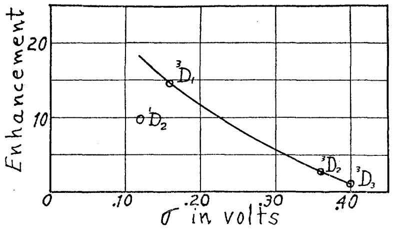

FIG. 1. Curve showing the relation between the relative enhancement of the d^9s copper levels and the energy discrepancy with neon ions.

The corresponding set of levels for the gold spark spectrum falls just below the helium ionization potential. A study of the enhancement of these levels was also made. The analysis of the gold spectrum used was that given by McLennan and McLay,[8] with the low term given by Sawyer and Thomson.[9] The results obtained are given in Table II. The 2995 line was given the same intensity value in the two discharges. The wide discrepancy in the value of the enhancement of the 2822.90 line from the last level in Table II is typical of a tendency toward an "over enhancement" of very strong lines. The error is probably in the experimental measurements. The preference for the $^3D_1$ level over the $^1D_2$ in spite of its greater energy discrepancy may be noted from the relative enhancements.

TABLE II. *Gold spark lines enhanced in the helium arc.*

Line	Initial level	Intensity in spark	Intensity in helium	Enhancement	Energy discrepancy (volts)
2995.00	$(d^97s)^3D_3$	4.4	4.4	1.0	1.92
2802.20		8.8	10.0	1.1	
2954.43	$^3D_2$	3.3	1.8	0.54	1.87
2838.03		3.0	1.6	0.53	
2918.40	$^3D_1$	1.2	31	26	0.37
2847.09		1.35	36	27	
2616.56		0.83	19	23	
2893.41	$^1D_2$	1.8	36	20	0.33
2822.70		3.5	96	27	
2533.69		1.1	22	20	

The aluminum spark spectrum has a number of levels in close resonance with the neon ionization potential, the excitation of which has been reported by Frerichs.[7] Table III contains a list of the results obtained by the writers for this case. A value of the enhancement of the

TABLE III. *Aluminum spark lines enhanced in the neon arc.*

Line	Initial level	Intensity in spark	Intensity in neon	Enhancement	Energy discrepancy (volts)
2475.26	5^1P	0.55	6.7	12.2	0.022
3315	5^3P	0.00	15.8	>30	0.003
2631.55	4^1F	10.0	10.0	1.0	0.27
3587	4^3F	46	121	2.6	0.28

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[8] McLennan and McLay, Trans. Roy. Soc. Can. **22**, 103 (1928).

[9] Sawyer and Thomson, Phys. Rev. **38**, 2293 (1931).

group of 5^3P levels could not be obtained since the group of lines at 3315 did not appear in the spark. However, the line 2475 did appear with an intensity, on the scale used, of 0.55, so that the intensity of 3315 must be less than 0.5. Thus the enhancement of this group must be greater than 30. The greater enhancement of the 4^3F level than the 4^1F of practically the same energy discrepancy is another example of a preference for triplet over singlet levels.

The excitation of the silver spark spectrum by helium ions was also studied. In the spark spectrum of silver, as analyzed by Shenstone,[10] there are twenty-two levels lying between one-half volt and two volts below the ionization potential of helium. Four of these belong to the d^96s configuration and the others to the d^95d configuration. Only five of the latter were studied, however, as the others gave lines too far in the ultraviolet for intensity measurements. Table IV contains the results obtained. Table V gives results obtained with lines from some of the lower silver spark levels. These lines represent transitions to the d^95s group of levels, which are metastable. The results clearly show the effect of absorption by the metastable atoms in the spark.

We are as yet unable to explain the surprisingly large enhancement of the d^96s levels of silver as shown in Table IV. It was at first thought that the anomalous results were caused by the fact that these levels were not being directly excited, but were filled by transitions down from the d^96p group, which was found to be strongly excited on account of its close resonance with the helium ionization potential. The lines corresponding to these transitions would lie in the far red and near infrared regions. A search failed to show any trace of such lines in the spectrum of the hollow cathode discharge, although the ultraviolet lines corresponding to d^96p-d^95s transitions were very strong. Thus these transitions could not explain the abnormal population of the d^96s levels. It might be noted however that the actual excitation of these levels was much weaker than that of the levels excited in copper, gold or aluminum, as exposures of two to five minutes were found necessary to bring out the silver lines, while five to fifteen seconds were sufficient for the other metals.

TABLE IV. *Silver spark lines enhanced in the helium arc.*

Line	Initial level	Intensity in spark	Intensity in helium	Enhancement	Energy discrepancy (volts)
2934.24	$(d^96s)^3D_3$	4.5	102	22.7	2.06
2712.07		7.4	176	23.8	
2606.14		1.8	39	21.7	
2477.25		4.6	93	20.2	
2938.55	$(d^96s)^3D_2$	1.8	27	15.0	2.01
2902.09		1.9	31	16.3	
2799.70		3.2	53	16.5	
2681.38		2.4	38	15.8	
2580.77		4.6	79	17.2	
2920.07	$(d^96s)^3D_1$	1.3	9.0	6.9	1.49
2873.62		2.1	15.0	7.0	
2614.56		1.9	12.6	6.6	
2504.11		1.4	8.6	6.1	
2896.50	$(d^96s)^1D_2$	2.4	14.7	6.1	1.46
2815.57		2.0	12.6	6.3	
2756.48		4.1	25.5	6.2	
2453.31	$(d^95d)^3D_3$	5.5	16.0	2.9	1.23
2444.22	$^1D_2$	3.2	18.3	5.7	0.67
2429.65	$^3F_4$	7.3	25	3.4	1.18
2390.58	$^3F_2$	2.7	31	11.5	0.62
2420.11	$^1F_3$	5.1	56	11.0	0.62

An attempt was made to excite the $^1D_2$, $^1F_3$, and $^1P_1$ levels of the d^96p configuration of gold with neon ions, the energy discrepancies in this case being 1.59, 1.69 and 2.19 volts, respectively. None of the lines from these levels were excited in neon. Hence it was concluded that the probability of excitation of levels with such great energy discrepancies must be very small, too small to account for the strong excitation of the d^96s configuration of Ag^+ by helium ions. It will be noted from Table II that the d^97s $^3D_3$ level is more enhanced than is the $^3D_2$ of less energy discrepancy. This is another instance of anomalous results with levels of large energy discrepancy.

TABLE V. *Silver spark lines enhanced in the helium arc. The effect of absorption of ^3D lines in the spark is evident.*

Line	Upper level	Lower level	Intensity in spark	Intensity in helium	Apparent enhancement
2929.37	$5p^3P_2$	$5s^1D_2$	2.9	4.2	1.4
2437.81		$5s^3D_3$	17.8	128	7.2
2767.54	$5p^3F_3$	$5s^1D_2$	7.1	11.0	1.5
2413.23		$5s^3D_2$	15.9	84	5.3
2660.49	$5p^3P_1$	$5s^1D_2$	4.1	4.7	1.1
2506.63		$5s^3D_1$	6.3	9.4	1.5

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[10] Shenstone, Phys. Rev. **31**, 317 (1928).

The results obtained with the lower spark levels of silver, Table V, are interesting, as they show that any considerable amount of absorption by a particular level will appear in the results. Thus the relatively greater enhancement of lines ending in the lower ^3D levels, particularly the $^3D_3$ and $^3D_2$ levels, than lines from the same upper level ending in the higher ^1D level is due to the absorption of lines ending in the ^3D levels in the spark. The explanation of these results must be that there is a higher population of the metastable levels in the condensed spark than in the low-voltage arc. If we assume that the population in the arc is so low that absorption in the arc may be neglected, we can obtain a value for the temperature of the spark, from the relative absorption by the different levels. We have $n_1/n_2=(g_1/g_2)e^{(E_2-E_1)/kT}$ where n_1 and n_2 are the populations of two states, E_1 and E_2 are the energies of these states, and g_1 and g_2 their respective statistical weights. Using the $^3D_3$ and $^3D_1$ levels and adjusting for the small difference in the two ratios for the $^1D_2$ level, we get $T=13{,}000°\mathrm{K}$. The weights used in this calculation were $2j+1$. Using the $^3D_2$ and $^3D_1$ levels, we get $T=8000°\mathrm{K}$. These values are not very close, but are of the same order of magnitude. The populations of the $^3D_2$ and $^3D_3$ levels appear from the results to be very nearly proportional to their statistical weights, which gives $T=\infty$. These levels are close together, however, so that a small change in the ratio would make a large change in the value obtained for the temperature.

In addition to the levels given above, a number of new levels of the silver spark spectrum were found to be enhanced by helium. These belong to the (d^96p) configuration, and lie close to the helium ionization potential. The lines are all in the far ultraviolet, and were photographed with a one meter vacuum grating from a hollow cathode source. A considerable number of lines were found which seemed to belong to this group, but their classification has not been completed. Table VI gives a few of the levels, which were tentatively identified. The three terms given in the table are the only ones which will combine with the low d^{10} term. There should be nine others combining with the terms of the d^95s configuration, and the observed lines which have not been analyzed will probably account for most of these levels.

TABLE VI. *New levels in silver spark spectrum.*

		(d^96p)	
	$^3P_1$ 132,835	$^1P_1$ 136,831	$^3D_1$ 137,221
(d^95s) $^3D_3$ 39,164			
$^3D_2$ 40,741	$I=6$ 92,096	$I=1$ 96,083	——
$^3D_1$ 43,739	——	Coincides with 2×537.12(He)	$I=3$ 93,486
$^1D_2$ 46,045	$I=7$ 86,790	$I=2$ 90,787	——
(d^{10}) $^1S_0$ 0.0	$I=8$ 132,835	$I=6$ 136,831	$I=1$ 137,221

A similar set of levels has also been observed in the gold spark spectrum, with lines in the same wave-length region. These levels belong to the d^97p configuration. The analysis has not been completed as yet, but enough of the expected frequency differences have been observed to show definitely that this configuration is involved. The levels lie very close to the helium ionization potential.

IV. GENERAL DISCUSSION

It has been assumed in this investigation that the mean life of the states excited by impacts of the second kind is so short that the relative intensities of the lines gave us the relative numbers of atoms originally excited to the various levels. If this is not the case in any instance, and the time is sufficient for some kind of distribution, as, for example, a Maxwell-Boltzmann distribution, to be effected, the analysis followed in this paper is not valid for that case.

In this work, an attempt has been made to find the importance of various factors affecting the action cross section for collisions of the second kind between rare gas ions and metallic atoms. No attempt has been made to compare the results of collisions between different types of atoms, but the relative cross section for the excitation of different levels of the same atom has been studied. The original aim of the investigation was to find the relation between energy discrepancy and action cross section, but the results indicate that other factors are also very important. Thus, in the cases of copper, gold and aluminum, where both singlet and triplet levels are strongly excited, there seems to be a preference for the triplet levels. This preference is most strongly marked in the lighter elements, copper and aluminum, but it is also quite apparent in gold.

This effect is not the one predicted by Wigner[4] although it bears some resemblance to it. From symmetry considerations, Wigner predicted that there should be a tendency for the conservation of electron spin in collisions of the second kind. The rule which results from this may be expressed as follows. Let n_1 be the number of electrons belonging to the first particle before the collision and n_2 the number belonging to the second. Some of these will be paired so that their spins cancel. Let z_1 and z_2 be the respective numbers of such electron pairs. Then the multiplicity of the state of the first particle before the collision will be given by n_1-2z_1+1 with a similar expression for the second particle. Wigner's rule states that the total number of pairs in the two particles after the collision is likely to have a value between z_1+z_2 and the smaller of the two numbers $n_1+z_2-z_1$ and $n_2+z_1-z_2$. If we apply this rule to the case of the collisions between copper atoms and neon ions, we have the following data: n_1 (for copper) $=29$; $z_1=14$ since the low term of the copper atom is a doublet term. n_2 (neon ion) $=9$, $z_2=4$. Applying the rule we find that the total number of pairs after the collision should lie between 18 and 19 (these numbers are included in the range). After the collision, the neon returns to its normal state, and the copper is ionized and excited. Since the neon contains five pairs in its normal state we should expect either thirteen or fourteen pairs in the copper ion. Thirteen pairs leave two unpaired electrons, or a multiplicity of three, fourteen pairs leave none unpaired, or a multiplicity of one. Thus Wigner's rule offers no choice between the singlet and triplet levels. A case in which Wigner's rule does apply has been discussed by Beutler and Eisenschimmel,[11] who found that the rule was supported by experimental results.

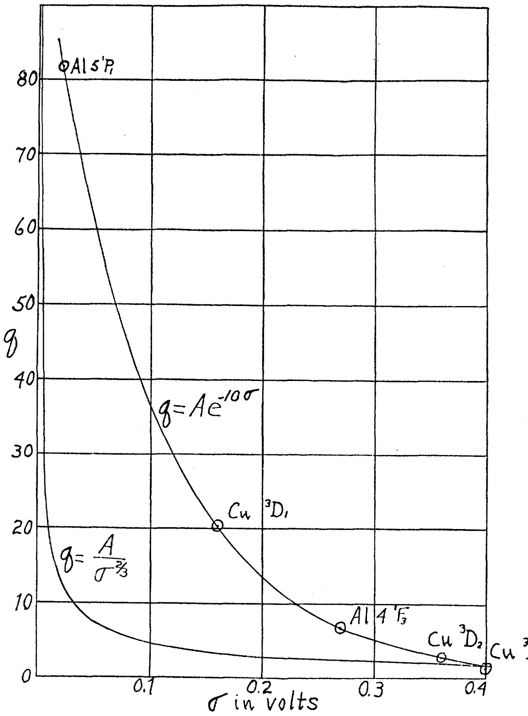

FIG. 2. The relation between action cross section and energy discrepancy.

The experimental results are not sufficient as yet to justify any attempt to formulate a relation between energy discrepancy and action cross section. Fig. 2 shows a graph between energy discrepancy and enhancement for the three triplet levels of copper and the two singlet levels of aluminum. The measurements on other levels cannot be included in this graph because they are individual cases; there are no levels with which they can be compared. The assumption has been made in drawing this graph that the law for singlet levels is the same as that for triplet levels, except for a constant factor. The experimental results are compared with the formula given by Kallman and London[3] though their theory was not formulated for the type of impacts here investigated, and with the formula $q=ae^{-\alpha\sigma}$ where $\sigma=$ energy discrepancy in electron volts, and $\alpha=10$.

In conclusion the authors wish to thank Professor G. E. Uhlenbeck for his interest in the problem, and a great deal of valuable advice, and Professor R. A. Sawyer for his assistance in the work with the vacuum grating spectrograph.

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[11] Beutler und Eisenschimmel, Zeits. f. physik. Chem. **10B**, 89 (1930).