SENSITIZED FLUORESCENCE IN A MIXTURE OF MERCURY AND CADMIUM VAPORS

by

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INTRODUCTION

When a mixture of two different vapors is illuminated by radiation that can be absorbed by only one of the vapors, the atoms of the non-absorbing vapor can be observed to fluoresce. This luminescence is termed sensitized fluorescence.

To better understand this phenomena, consider a hypothetical mixture of two different vapors, A and B. Let the atoms of vapor A have an energy level E_a as the first excited level above their normal state, while the atoms of B have as their corresponding level an energy state designated E_b. Assume that E_a is greater than E_b, and further, that the incident frequency, f_a, times Planck's constant is equal to E_a. Then, as atom A absorbs the incident radiation, it will change to an excited state, A*. If the half life of the excited state of A* is of like order of magnitude as the time between collisions between atoms A and B, it will be probable, by collisions of the second kind, for the energy of A* to be transferred to atom B. The energy difference, $E_a - E_b$, will be divided between the colliding atoms in the form of kinetic energy. The atom B* can then emit energy of a new frequency, f_b.

It is also possible for kinetic energy to combine with the energy of an excited atom to excite a second atom to a higher energy level. If, for example, vapor B in the above mentioned mixture were replaced by a vapor C, that has an atomic energy level, E_c, which is greater than E_a, it would be possible for the quantum, hf_a, to combine with thermal energy to excite the atom C to E_c, its lowest excited state. The energy difference here, $E_c - E_a$, would have to be obtained from the relative kinetic energy of the two atoms. This emission frequency, f_c, from atom C* would be different from either f_a or f_b.

Cario and Franck (1) sought to verify these hypotheses experimentally in 1924. They reported evidence which substantiated both predictions. The purpose of this research was to confirm their results and to obtain more quantitative information with the aid of improved techniques and equipment.

THEORY

Cario and Franck performed their first experiments using mercury and thallium vapors. Their experimental arrangement consisted of two reservoirs connected to an absorption vessel. In one reservoir a sample of mercury was deposited. The other held thallium. These reservoirs were in separate ovens, to enable the experimenter to control the temperature, and hence, the vapor pressure of the materials. The absorption vessel was placed in a third oven which was capable of supplying the thermal energy necessary to excite the atoms to the states lying higher than the quantum energy of incident radiation. The mixture of the two vapors in the absorption vessel was irradiated by light from a water cooled mercury arc lamp. The principal irradiating line was the 2537 A resonant line arising from the mercury $6^1S_0 - 6^3P_1$ transition. It was essential that this line be unreversed. The reradiated light was dispersed and detected with the aid of a quartz spectrograph.

Sensitized fluorescence was observed from thallium levels lying both above and below the 4.86 volt level of the mercury resonant line. However, the intensity ratios for some of the lines were not as had been expected. This was attributed to the fact that metastable states which

EXPLANATION OF PLATE I

Fig. 1. Energy level diagram of mercury.

Fig. 2. Energy level diagram of cadmium.

PLATE I

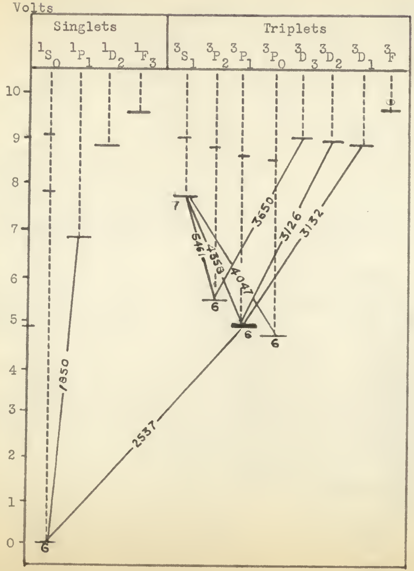


Fig. 1

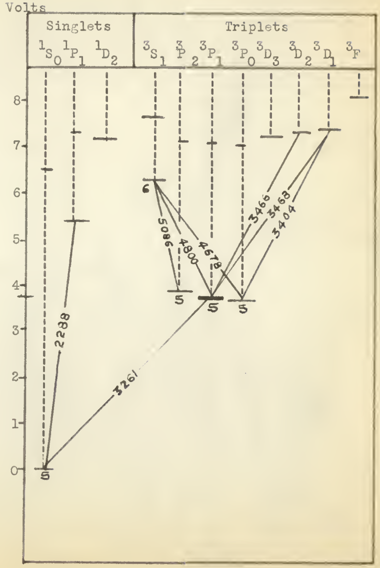


Fig. 2

could be excited thermally were present in thallium. The next step was to replace the thallium by cadmium since it has no such low lying metastable states. With the main oven at 400°C, they observed only the cadmium 3261 A resonant line from the $5^1S_0 - 5^3P_1$ transition. At 800°C, the triplet emanating from the 6^3S_1 level of cadmium as well as the 3261 A line was observed on the spectrograms. The possibility of exciting this level by stepwise absorption was ruled out, as the same results were obtained when a monochromator was used to pass only the mercury resonant line as the exciting radiation. Referring to Plate I (Mitchell and Zemansky, 2), it can be seen that the 6^3S_1 level of cadmium lies at 6.3 electron volts. This means that 1.4 electron volts of thermal energy was supplied by the main oven to excite the atom to this level. This was cited as evidence supporting the contention that thermal and quantum energy can cooperate in exciting higher levels.

The main improvement in performing the experiment again as described in this paper was the substitution of a photomultiplier for photographic film as the detecting device. This has the obvious advantage of observing the results while performing the experiment as well as saving time in focusing. An additional objective was to obtain temperature versus intensity graphs for the triplet of cadmium.

APPARATUS AND TECHNIQUE

The source of the 2537 A radiation used in this research was a Sylvania U-shaped germicidal lamp. The 2537 A resonant line was predominant, although the mercury triplet consisting of the 4047, 4358, and 5461 A lines was present in measurable intensity. A complete spectrum is listed with the results. This radiation was focused on the absorption vessel by a fused quartz lens of focal length 16.3 cm. The lens was supported by a horizontally mounted rod. The distance from a reference point on the rod to the point of focus for the 2537 A line was determined by focusing the same on a fluorescent screen while the visible light was filtered out. This simplified the focusing procedure in the research. The combined optical system is shown in the center of the photograph on Plate II.

The construction of the ovens was the most time consuming part of preparing the experimental equipment, hence considerable attention has been given to this item. The heater coils were of Chromel-A wire, closely would around a 1.5 mm. rod which was mounted in the lathe. After being removed from the lathe, the coil was elongated to approximately four times its original length. The coil was first wrapped around an alundum core, which was helically grooved, then tied in place with a string. The coil was then carefully washed with alcohol to remove any contamination which might cause corrosion upon heating, and inserted into a hollow cylindrical form which had been poured from refractory concrete. This sheath served to hold the coil in position after the string had burned away as well as to separate the coils from asbestos. The sheath, core, and coil were supported between two plates of transite which were bolted together. The bolts also served as electrodes. The system was further insulated thermally by a mixture of asbestos paste which when dried, lent support to the oven.

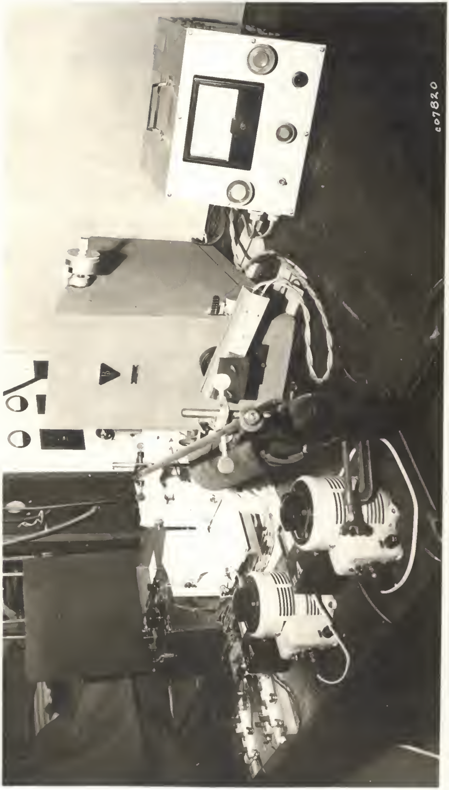
Plate III shows the ovens. The two smaller ones were built as described above. The one on the left contains a quartz observation window in the end as a means of determining the amount of material in the oven

EXPLANATION OF PLATE II

Apparatus used in experiment.

The following are shown in the photograph: Variable transformers, ammeters, light source and shielded lens, ovens, monochromator, photovolt, and temperature measuring potentiometer.

PLATE II



EXPLANATION OF PLATE III

Fig. 1. Photograph of front view of ovens and Cd reservoir.

Fig. 2. Photograph of diagonal view of ovens and Hg reservoir.

PLATE III

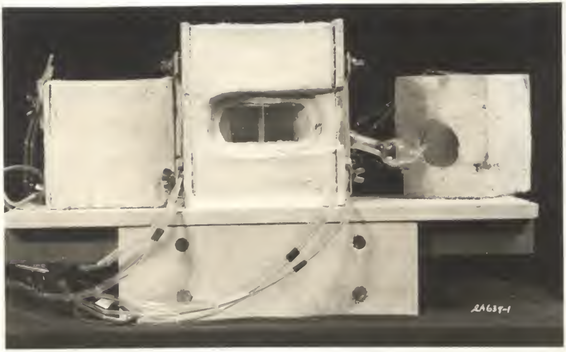


Fig. 1

Fig. 2

without removing the oven. The main oven in the center has two quartz windows in the side through which the incident and the sensitized fluorescence radiations passed. To help compensate for the heat losses through the window area, the heating coil was compressed by a factor of three at the ends and center of the aperture. Fig. 2 of Plate III shows how the thermocouples were rigidly mounted to facilitate measurement of the temperature at the same point on the reservoirs. Since the auxiliary ovens could not always be in the same position relative to the reservoirs, this was necessary for reproducible temperature results.

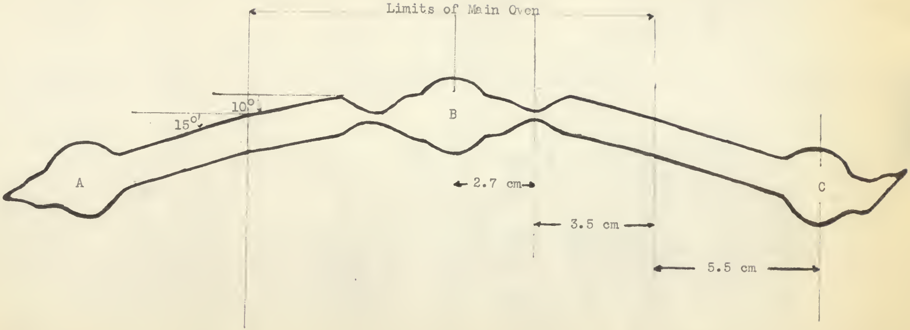
The quartz cell is shown in Plate IV. The bulb in the center is the absorption vessel. At the left end is the mercury reservoir; at the right is the reservoir containing cadmium. The constrictions serve to decrease the rate of diffusion through the tube. They are located within the limits of the main oven. Since the main oven is maintained at the highest temperature, this minimizes the possibility of condensation occurring at the constriction and hence clogging the vessel.

The tube connecting the vessel to the reservoir is bent downward to cause the mercury to flow into the reservoir where it can be more readily observed. After the quartz vessel had been blown to the proper shape, it was attached to a vacuum system and evacuated. The vacuum system consisted of a Welch Duo-seal fore pump and a Wisconsin type mercury diffusion pump. A Bayard-Alpert ionization guage was used to measure the pressure. One liquid nitrogen trap separated the guage from the diffusion pump. Another trap was placed between the guage and the container being evacuated. Phosphorous pentoxide in the system absorbed water vapor which might have been present. The cell was outgassed under vacuum at 800°C for 24 hours.

EXPLANATION OF PLATE IV

Sketch of the quartz absorption vessel and reservoirs.

PLATE IV



After 0.7 cm^3 of both mercury and cadmium were distilled into the system, it was evacuated down to approximately 2×10^{-6} mm. of mercury, outgassed again, and sealed under vacuum.

The light emerging from this vessel was dispersed and its wavelength measured with a Bausch and Lomb, 500mm, grating-type monochromator. Light traps were used to prevent light from the source reaching the monochromator directly. A model 1P28 photomultiplier tube was used as the light detecting device. This tube was mounted in the receptor of a Photovolt multiplier photometer which is essentially a D.C. amplifier. The temperatures were measured with chromel-alumel thermocouples in conjunction with a Leeds and Northrup potentiometer indicator. The items mentioned above are shown in Plate II.

One of the more difficult problems in the techniques was the focusing of the system. The method found best was to first position the optical system the premeasured distance from the reference mark to the absorption vessel. The monochromator was then moved until a maximum 2537 A intensity was observed. The optical system and monochromator were then alternately moved until the 2537 A line could no longer be intensified. The monochromator was then set on the 3261 A line of cadmium and the procedure repeated until the cadmium resonant line could not be made more intense. The system was then assumed to be in focus.

To ascertain that the triplet was not excited by stepwise absorption, a black wire screen which diminished the intensity by a factor of one-half was to have been used. If stepwise absorption were the responsible excitation mechanism, the intensity would be reduced by one half when the screen was placed between the monochromator and the absorption cell and by one fourth when interposed between the ultra-violet source and the absorption cell.

The second order ghost from the 2537 A line was so intense that it masked the 5086 A line from the cadmium triplet. This ghost was eliminated, when scanning for this line, by blocking the 2537 A line from the monochromator with a pyrex glass plate.

EXPERIMENTAL RESULTS

Tables 1 and 2 show a typical source spectrum and the thermal background from the main oven at 800°C. It was not necessary to correct the mercury lines in the following data for this background, since the mercury lines in the region where this background was significant were reflected lines. However, the cadmium line intensities listed are corrected for this background.

In Tables 3 through 8, T_m represents the average temperature of the main oven as determined by two thermocouples, one on either side of the absorption cell. T_{cd} and T_{hg} are the temperatures of the reservoirs for cadmium and mercury, as determined by a thermocouple in contact with each reservoir. These temperatures can be correlated to equilibrium vapor pressures with the aid of the graph on Plate V. (3) The subscripts after the current symbol, I, refer to the cadmium, mercury and main ovens.

The two parts of Table 3 were intensity measurements made when the constriction between the mercury reservoir and the absorption cell was about 2 mm. in diameter. The top set was taken with the monochromator slits opened to approximately 0.80 mm., and the bottom set when the slits were opened to 0.40 mm.. The data in Tables 4 through 8 were taken with the constriction mentioned above closed down to approximately 0.5 mm. in diameter. Since the 0.40 mm. slit widths were optimum for both intensity and resolution, the data on the pages following Table 3 were taken with these apertures.

In the earlier work, an attempt to find the 5086 A line of the cadmium triplet was not always made, since it would have been masked by the second order appearance of the 2537 A line of mercury. Later, the previously mentioned technique with the pyrex plate was used to eliminate this obstacle.

Table 1. Irradiating spectrum.

Wavelength in angstroms	Relative intensity
2537	23,000
2752	32
2894	62
2967	33
3132	1,100
3341	110
3650	150
4047	3,300
4358	5,300
4916	24
5074	*
5461	2,000

* The line appearing at 5074 was the second order appearance of the 2537 resonant line.

Table 2. Background at 800°C.

Wavelength in angstroms	Relative intensity
3500	0
3600	0
3700	0
3800	0
3900	0
4000	0
4100	0
4200	0
4300	0.2
4400	0.4
4500	1.0
4600	1.2
4700	1.8
4800	3.0
4900	4.0
5000	5.8
5100	7.6
5200	10
5300	13
5400	16
5500	19
5600	22.5
5700	25.2
5800	28
5900	28

Table 3. Variation of line intensities with time and temperature.

10 min. time interval	Temperature of ovens in ^oC			Relative intensity										Oven current in amperes		
				Mercury lines						Cadmium lines						
	T_m	T_{cd}	T_{hg}	2537	3132	3650	4047	4358	5461	3261	4678	4800	5086	I_{cd}	I_{hg}	I_m
1	795	125	107	770	13	30	84	230	220	2	0	0	0	0	0	7.0
2	811	152	97							5	0	0	*	0	0	7.0
3	826	172	95	575	13	30	84	230	275	52	0	0		0	0	7.0
4	831	175	135							26	0	0		0	0	6.8
5	823	182	102	490	12	29	83	220	240	18	0	0		0	0	6.8
6	818	182	100							7	0	0		0	0	6.8
7	820	196	127	420	12	29	83	230	250	4	0	0		1	0	6.8
8	821	207	122							6.5	0	0		1	0	6.8
9	821	209	110	410	12	28	82	225	245	7.5	0	0		1	0	6.8
10	824	250	114							70	0	0		2	0	6.8
11	829	280	120	500	21	42	120	300	300	46	0	0		2	0	6.8
12	830	293	103							3.5	0	0		2	0	6.8
13	833	313	140	300	23	47	130	320	300	1.0	0	0		2.5	0	6.8
14	824	338	93							2.0	0	0		2.5	0	6.8
1	851	204	82	170	5.8	19	65.5	172	96	0.4	0	0	0	0	0	6.6
2	850	210	88							3.0	0	0	*	0	0	6.6
3	840	219	87	212	6.3	19	64	165	92	11.5	0	0		0	0	6.4
4	837	223	89							14.0	0	0		0	0	6.4
5	837	228	88	225	6.6	19	65	160	93	14.0	0	0		0	0	6.4
6	834	240	93							22	0	0		0	1.0	6.4
7	834	265	91	220	6.8	20	68	175	93	19.5	0	0		0	1.0	6.4
8	834	266	86							15.5	0	0		0	1.0	6.4
9	834	295	91	210	6.7	20	68	170	93	16.0	0	0		0	1.5	6.4
10	834	311	89							5.0	0	0		0	1.5	6.4
11	839	331	93							0	0	0		0	1.5	6.4

* Not measured below here.

Table 4. Variation of line intensities with time and temperature.

15 min. time interval	Temperature of ovens in °C			Relative intensity: Mercury lines						Relative intensity: Cadmium lines				Oven current in amperes		
	T_m	T_{cd}	T_{hg}	2537	3132	3650	4047	4358	5461	3261	4678	4800	5086	I_{cd}	I_{hg}	I_m
1	788	86	81	510	16	26	66	160	64	0	0	0	0	0	0	6.1
2	808	139	83	460	15	28	65	170	71	0	0	0	0	1	0	6.3
3	812	202	81	370	16	28	67	170	74	0.1	0	0	0	1	0	6.2
4	813	222	83	340	16	28	66	170	75	0.1	0	0	0	1	0	6.2
5	816	258	84	330	16	28	66	170	75	13	0	0	0	1.5	0	6.2
6	818	274	83	320	16	29	67	170	74	58	0	0	0	1.5	0	6.2
*7	820	285	86	250	14	28	71	200	86	45	0	0	0	1.5	0	6.2
8	819	288	86	250	15	30	75	210	89	45	0	0	0	1.5	0	6.1
9	819	294	91	260	14	29	73	200	86	42	0	0	0	1.5	0	6.1
10	816	294	87	250	15	29	75	200	87	40	0	0	0	1.5	0	6.1
11	815	297	88	250	14	29	74	200	87	36	0	0	0	1.5	0	6.1
12	816	297	83	270	15	28	74	200	86	33	0	0	0	1.5	0	6.1
13	816	303	84	250	14	29	74	190	87	51	0	0	0	2.0	0	6.1
14	818	336	86	230	14	28	73	200	88	71	0	0	0	2.0	0	6.1
15	820	345	88	220	14	28	73	200	88	75	0	0	0	2.0	0	6.1
16	820	353	88	220	14	28	72	200	88	75	0	0	0	2.0	0	6.1
17	820	360	86	230	14	28	73	190	88	75	0	0	0	2.0	0	6.1
18	821	360	86	250	14	28	73	190	88	73	0	0	0	2.0	0	6.1
19	821	362	86	250	14	28	72	190	89	41	0	0	0	2.0	0	6.1
20	823	362	86	260	14	28	72	190	88	18	0	0	0	2.0	0	6.1
21	823	386	86	250	14	28	72	190	89	45	0	0	0	2.3	0	6.1
22	824	400	86	260	14	28	72	190	90	18	0	0	0	2.3	0	6.1
23	823	405	83	260	14	27	72	190	89	6	0	0	0	2.3	0	6.1
24	815	410	81	270	15	29	73	200	85	2	0	0	0	2.3	0	6.1
25	810	410	81	280	14	28	73	190	84	1	0	0	0	2.3	0	6.0
26	817	426	82	270	14	28	72	190	86	1	0	0	0	2.5	0	6.1
27	822	433	82	280	14	27	72	190	86	0.5	0	0	0	2.5	0	6.1
28	821	437	83	280	14	27	73	200	88	0.5	0	0	0	2.5	0	6.1
29	823	438	83	290	14	27	73	200	89	0.7	0	0	0	2.5	0	6.1

* System was refocused preceeding this reading.

Table 5. Variation of line intensities with time and temperature.

15 min. time interval	Temperature of ovens in °C			Relative intensity										Oven current in amperes		
				Mercury lines						Cadmium lines						
	T_m	T_{cd}	T_{hg}	2537	3132	3650	4047	4358	5461	3261	4678	4800	5086	I_{cd}	I_{hg}	I_m
1	789	108	81	660	20	45	120	210	94	0	0	0	0	0	0	6.8
2	791	130	81	500	12	33	85	220	92	0	0	0	0	1	0	6.8
3	797	177	83	430	12	32	87	220	85	0	0	0	0	1	0	6.8
4	799	202	85	340	13	33	87	230	87	0.2	0	0	0	1	0	6.8
5	800	220	86	310	12	32	87	230	85	0.4	0	0	0	1	0	6.8
6	802	230	83	310	13	33	80	220	86	1.5	0	0	0	1	0	6.8
7	802	261	86	450	20	40	100	250	84	68	0	0	0	1.5	0	6.8
8	803	270	89	400	19	40	100	240	83	81	0	0	0	1.5	0	6.8
9	803	280	89	470	20	48	120	290	97	88	0	0	0	1.5	0	6.8
10	803	289	88	480	25	47	120	290	97	20	0	0	0	1.5	0	6.8
11	800	290	88	490	24	47	120	290	96	25	0	0	0	1.5	0	6.8
12	800	290	88	490	25	47	120	280	96	28	0	0	0	1.5	0	6.8
13	800	290	88	490	23	46	120	280	96	31	0	0	0	1.5	0	6.8
14	800	292	88	490	24	46	120	280	96	36	0	0	0	1.5	0	6.8
15	800	292	88	490	23	46	120	280	95	40	0	0	0	1.5	0	6.8
18	800	300	88	540	25	46	120	270	94	42	0	0	0	1.5	0	6.8
19	800	326	88	490	24	46	120	260	93	64	0	0	0	2.0	0	6.8
20	800	345	88	480	25	45	110	260	92	95	0	0	0	2.0	0	6.7
21	800	353	83	490	24	44	110	260	92	95	0	0	0	2.0	0	6.7
22	718	360	83	450	23	48	120	330	120	100	0	0	0	2.0	0	6.7
23	808	367	83	490	23	50	130	340	120	70	0	0	0	2.0	0	6.8
24	810	368	81	480	23	50	130	330	110	25	0	0	0	2.0	0	6.8
25	683	365	76	490	23	49	140	340	120	8	0	0	0	2.0	0	3.4
26	689	393	117	340	12	37	87	230	90	15	0	0	0	2.5	0	4.0
27	686	415	120	340	12	30	88	230	92	14	0	0	0	2.5	0	4.0
28	687	417	81	320	11	30	86	230	91	4	0	0	0	2.4	0	4.0
29	684	419	101	320	11	33	89	240	91	2	0	0	0	2.4	0	4.0

Table 6. Variation of line intensities with time and temperature.

15 min. time interval	Temperature of ovens in °C			Relative intensity										Oven current in amperes		
				Mercury lines						Cadmium lines						
	T_m	T_{cd}	T_{hg}	2537	3132	3650	4047	4358	5461	3261	4678	4800	5086	I_{cd}	I_{hg}	I_m
1	802	72	81	400	9	19	50	130	67	0	0	0	0	0	0	6.2
2	811	142	85	350	9	19	50	130	68	0	0	0	0	1.0	0	6.2
3	818	190	88	270	9	19	49	130	69	0.1	0	0	0	1.0	0	6.2
4	821	207	90	240	8	18	48	120	69	0.1	0	0	0	1.0	0	6.2
5	823	224	94	220	8	19	49	120	70	0.2	0	0	0	1.0	0	6.1
6	823	229	94	260	8	18	45	110	63	0.2	0	0	0	1.0	0	6.1
7	818	256	97	260	9	18	45	110	61	19	0	0	0	1.5	0	6.1
*8	816	273	97	250	9	25	61	150	74	57	0	0	0	1.5	0	6.1
9	816	277	97	250	13	24	61	150	75	34	0	0	0	1.5	0	6.1
10	815	280	88	230	13	25	61	150	75	47	0	0	0	1.5	0	6.1
11	815	283	93	230	13	25	61	150	74	42	0	0	0	1.5	0	6.1
12	817	286	93	220	13	25	60	150	77	26	0	0	0	1.5	0	6.1
15	825	293	100	220	12	24	60	150	77	19	0	0	0	1.5	0	6.1
16	825	319	107	200	12	24	59	150	76	38	0	0	0	2.0	0	6.1
17	825	333	103	200	13	24	60	140	76	45	0	0	0	2.0	0	6.1
18	825	341	103	200	13	24	59	140	75	50	0	0	0	2.0	0	6.1
19	825	350	103	200	13	24	59	140	76	54	0	0	0	2.0	0	6.1
20	825	355	100	200	12	23	58	140	75	53	0	0	0	2.0	0	6.1
21	825	360	96	210	13	24	59	140	76	54	0	0	0	2.0	0	6.1
22	825	376	96	210	13	23	58	140	76	53	0	0	0	2.3	0	6.1
23	825	390	89	220	12	23	56	140	75	46	0	0	0	2.3	0	6.1
24	825	397	84	220	12	23	55	140	75	19	0	0	0	2.3	0	6.1
25	825	400	100	220	12	23	55	140	74	4	0	0	0	2.3	0	6.1
26	826	400	96	220	12	22	55	140	74	1	0	0	0	2.3	0	6.1
27	826	402	98	220	12	22	54	140	74	0.7	0	0	0	2.3	0	6.1
28	826	400	98	210	12	22	55	140	73	0.5	0	0	0	2.3	0	6.1
29	826	405	97	230	12	22	55	140	73	0.5	0	0	0	2.3	0	6.1

* Refocused

Table 7. Variation of line intensities with time and temperature.

15 min. time interval	Temperature of ovens in °C			Relative intensity										Oven current in amperes		
				Mercury lines						Cadmium lines						
	T_m	T_{cd}	T_{hg}	2537	3132	3650	4047	4358	5461	3261	4678	4800	5086	I_{cd}	I_{hg}	I_m
1	843	386	83	370	14	28	73	190	95	1	0	0	0	2.3	0	6.3
2	831	396	124	330	13	27	71	180	91	1.1	0	0	0	2.3	0	6.1
3	829	402	124	330	13	27	72	180	89	1.6	0	0	0	2.3	0	6.1
4	828	402	123	330	14	27	71	180	89	1.5	0	0	0	2.3	0	6.1
5	828	419	169	300	13	26	70	180	88	1.5	0	0	0	2.5	0	6.1
6	828	426	180	290	13	26	70	180	88	1.8	0	0	0	2.5	0	6.1
7	828	428	189	280	13	26	70	170	87	1.7	0	0	0	2.5	0	6.1
8	831	435	224	220	13	26	68	180	89	0.5	0	0	0	2.5	0	6.1
9	836	438	242	200	13	26	68	170	88	0.4	0	0	0	2.5	0	6.1
10	836	443	259	190	13	26	68	170	86	0.6	0	0	0	2.5	0	6.0
11	834	440	263	180	13	25	66	170	86	1.0	0	0	0	2.5	0	6.0
12	834	440	270	390	18	28	60	130	66	1.0	0	0	0	2.5	0	6.0
1	783	370	73	520	18	28	60	130	56	0.5	0	0	0	2.5	0	6.0
2	800	388	78	490	18	27	58	130	59	0.8	0	0	0	2.5	0	6.1
3	812	398	78	480	18	27	59	130	60	0.9	0	0	0	2.4	0	6.1
4	818	412	85	480	18	26	57	130	64	0.6	0	0	0	2.4	0	6.1
5	822	414	117	470	18	26	56	130	64	0.6	0	0	0	2.4	0	6.1
6	822	416	116	470	16	25	56	130	63	0.5	0	0	0	2.4	0	6.1
7	823	417	122	470	16	26	56	130	63	0.5	0	0	0	2.4	0	6.1
8	817	419	165	470	16	26	57	130	62	0.9	0	0	0	2.4	0	6.0
9	817	417	174	470	17	26	57	130	60	1.0	0	0	0	2.4	0	6.0
10	814	419	182	460	17	26	56	130	61	1.0	0	0	0	2.4	0	6.0
11	817	419	204	420	17	25	56	130	61	0.6	0	0	0	2.4	0	6.0
12	821	421	236	390	17	25	55	130	62	0.3	0	0	0	2.4	0	6.0
13	823	424	249	360	17	25	55	130	62	0.5	0	0	0	2.4	0	6.0
14	823	428	286	350	17	25	55	130	63	1.0	0	0	0	2.4	0	6.0

Table 8. Variation of line intensities with time and temperature.

15 min. time interval	Temperature of ovens in °C			Relative intensity										Oven current in amperes		
				Mercury lines						Cadmium lines						
	T_m	T_{cd}	T_{hg}	2537	3132	3650	4047	4358	5461	3261	4678	4800	5086	I_{cd}	I_{hg}	I_m
1	822	402	79	230	11	21	53	130	72	0.9	0	0	0	2.3	0	6.1
2	825	390	107	230	11	21	52	130	71	0.3	0	0	0	2.3	0	6.1
3	825	400	112	220	11	21	51	130	71	0.4	0	0	0	2.4	0	6.1
4	825	407	143	210	11	21	51	130	70	0.5	0	0	0	2.4	0	6.1
5	825	412	145	210	10	20	51	130	70	0.5	0	0	0	2.4	0	6.1
6	825	412	189	200	10	20	50	120	69	0.8	0	0	0	2.3	0	6.1
*7	823	410	190	160	9	19	49	130	73	0.5	0	0	0	2.3	0	6.1
8	837	419	249	230	12	19	49	130	75	0.3	0	0	0	2.3	0.5	6.1
9	837	421	266	220	11	18	48	130	78	0.5	0	0	0	2.3	0.5	6.0
10	835	424	293	210	11	19	44	100	61	7	0	0	0	2.3	1.0	6.0
11	830	424	305	200	11	19	43	100	61	7	0	0	0	2.3	1.0	6.0
12	830	417	317	220	11	18	40	100	56	6	0	0	0	2.3	1.0	6.0
1	810	412	83	230	10	17	40	100	54	0.8	0	0	0	2.4	0	6.0
2	810	409	100	230	10	17	40	100	53	0.7	0	0	0	2.4	0	6.0
3	807	410	110	230	10	18	41	100	53	0.5	0	0	0	2.4	0	6.0
4	807	407	167	230	10	17	40	100	53	0.7	0	0	0	2.4	0	6.0
5	810	407	192	210	10	17	40	100	53	0.5	0	0	0	2.4	0	6.0
6	810	407	235	200	10	17	40	100	53	0.3	0	0	0	2.4	0.5	6.0
7	813	410	274	190	10	17	39	100	53	0.5	0	0	0	2.4	0.5	6.0
8	813	412	264	180	10	17	39	100	53	0.9	0	0	0	2.4	0.5	6.0
9	815	412	285	180	10	17	40	100	54	5	0	0	0	2.4	1.0	6.0
10	817	413	302	170	10	17	40	100	55	6	0	0	0	2.4	1.0	6.0
11	820	412	313	170	10	17	39	100	55	5	0	0	0	2.4	1.0	6.0
12	820	412	317	170	10	17	39	100	55	4	0	0	0	2.4	1.0	6.0
13	820	412	317	170	10	17	39	100	55	3	0	0	0	2.4	1.0	6.0
14	820	412	310	170	10	17	39	100	55	5	0	0	0	2.4	1.0	6.0

* Ovens were moved during adjustment.

DISCUSSION OF RESULTS

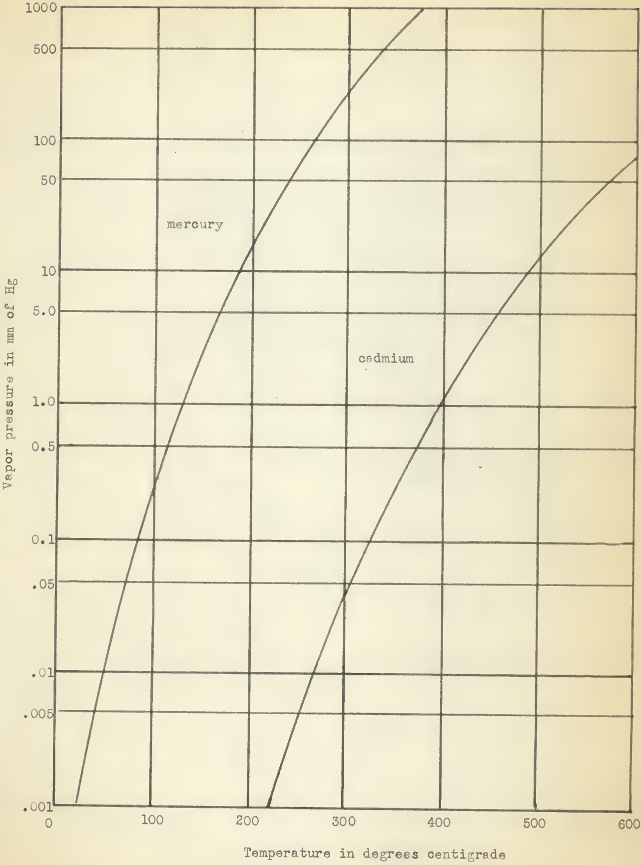
The lines of principal interest for this problem were those of cadmium. The 3261 A line of cadmium was observed to be moderately intense at times. It was found that the optimum initial conditions for its observation were when the mercury and cadmium were together in the reservoir which was to be heated. The runs in Tables 4, 5, and 6 were started by having both cadmium and mercury in the cadmium reservoir. The mercury reservoir was left in the open air. As the mixture in the cadmium reservoir was heated, both the mercury and cadmium vapor began to move out. At a temperature of 250°C, the cadmium vapor pressure was sufficient for the 3261 A line of cadmium to be observed. The results show that the line normally appeared more intense during a rapid temperature increase, which followed an abrupt increase in the current. After the temperature was reasonably stable, the intensity would decrease. No positive explanation is given for this action. However, it may be that the mercury, which has a high vapor pressure at these temperatures as indicated by the graph on Plate V, carried small particles of cadmium into the absorption cell as it rushed from the cadmium reservoir. These small cadmium particles would then be vaporized and furnish sufficient concentrations of cadmium vapor for the resonant line to be observed. As the cadmium reservoir temperature was further increased, this intensity pulsing was observed again. At 400°C, the intensity of the 3261 A line had diminished to near zero, and remained there even though cadmium remained in the heated cell and a relatively high mercury vapor pressure was present.

According to the literature, the optimum temperatures for sensitized fluorescence of mercury and cadmium are 400°C for the cadmium and 100°C for the mercury. Further literature research disclosed that the behavior

EXPLANATION OF PLATE V

Pressure vs. temperature curves for mercury and cadmium.

PLATE V


1000
500
100
50
10
5.0
1.0
0.5
0.1
.05
.01
.005
.001
0
100
200
300
400
500
600
mercury
cadmium
Vapor pressure in mm of Hg
Temperature in degrees centigrade

just described had been observed before by Mitchell, (4) when studying the polarization of sensitized fluorescence in mercury and cadmium vapors. His explanation was that the cadmium vapor carried the mercury vapor from the absorption cell with it, as it migrated to a colder reservoir. Due to the high vapor pressure of mercury at 400°C, it is reasonable to assume that little mercury would be left at equilibrium in the cadmium reservoir. The mercury vapor pressure would then be controlled by the reservoir whose temperature was between 80 and 100°C, where its equilibrium vapor pressure would be of the order of 1 mm. of mercury, as would be the vapor pressure of cadmium at 400°C. The non-equilibrium condition of the cadmium would cause streaming and a degree of pumping. Mitchell's explanation seems consistent with these results.

The constriction between the mercury reservoir and the absorption cell was reduced to one-fourth of its original diameter in an effort to decrease this pumping rate. The data in Tables 4 through 8 are typical of data taken after the smaller opening was in use. Still, at the optimum temperatures, the intensity of the cadmium resonant line was negligible. Some moderate intensities were obtained during the transient stages of heating. These intensities might possibly be exceeded if the optimum concentrations of the two vapors could be attained under equilibrium conditions.

Tables 7 and 8 are illustrative of data obtained while trying to find a mercury temperature which would neutralize this pumping action after the cadmium vapor had transported the mercury vapor out of the absorption cell. Only when the mercury temperature was near 300°C was the cadmium resonant line observed again, even then the intensity was low. In view of this low intensity and the fact that several mishaps had occurred near this mercury temperature, it was felt that it would be neither safe nor fruitful to continue at these temperatures.

The primary objective of this experiment was to obtain some quantitative measurements of the cadmium triplet. The intensities involved were so low that they were not discernible above the random fluctuations of the measuring device, which were less than one tenth of one unit. Considering the intensities of the observed cadmium resonant line, this is not altogether surprising. Franck and Cario calculated that only one part in 3×10^5 of all collisions have sufficient relative kinetic energy to supply the 1.4 ev energy difference necessary to excite the cadmium atom to the 6^3S_1 level. Since it is energetically possible for all collisions between excited mercury atoms and cadmium atoms to result in an excited cadmium atom, one would expect this ratio or a lower one for the intensities of the resonant line and the triplet.

The results also indicate some variation in the intensities of the mercury lines. These variations were not in general correlated to the results for cadmium. The intensity of the 2537 A line was due not only to resonance radiation, but also to scattering. The contribution of each of these phenomena to the total intensity is not known. The 3132 and 3650 A lines are attributable to scattering. The intensities of the 5416, 4358, and 4047 A lines from the source were moderately high. It is possible that these lines could be absorbed by excited mercury atoms in the 6^3P levels, to raise the atom to the 7^3S_1 level. Resonance radiation would result. The test for stepwise absorption was made. After correcting for the thermal background, the resultant intensities were the same whether the screen was placed in the incident or outgoing beam. The conclusion was that these were also scattered lines. The variation in the intensity of these lines can be attributed to two factors. First, the mercury source does not maintain a constant intensity output. Secondly, the geometry of the system changed slightly due to thermal expansion of the ovens and the quartz cell.

CONCLUSIONS

Two conclusions can be drawn from this experiment. Since the optimum conditions for sensitized fluorescence are to have equal vapor pressures, this experiment should be performed with the mercury at 100°C and the cadmium at 400°C. Due to the pumping action of the cadmium, this is not feasible with the present arrangement. The solution of the problem by Mitchell indicates that helium equal in pressure to 2 mm. of mercury should be added to the cell in future experiments of this nature. Secondly, the problem of insufficient intensities must be overcome. The present system is clearly inadequate in this respect. If a stronger mercury light source cannot be obtained, perhaps more than one source could be used to irradiate the absorption cell.

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LITERATURE CITED

(1) Cario, A. and J. Franck.
Uber sensibilisierte Fluoreszenz. Zeit. F. Phy. 17:202-212. 1923.

(2) Mitchell, A. C. G. and M. W. Zenmansky.
Resonance radiation and excited atoms. New York: Macmillan. 1934.

(3) Stull, Daniel R.
Vapor pressure of inorganic compounds. Ind. and Eng. Chem. 39:517. 1947.

(4) Mitchell, A. C. G.
Polarization of sensitized fluorescence. Journ. Frankl. Inst. 209:747-756. 1930.

SENSITIZED FLUORESCENCE IN A MIXTURE OF MERCURY AND CADMIUM VAPORS

by

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Franck and Cario have postulated that atoms can be excited to higher energy levels through a cooperative effort between quantum and kinetic energies during a collision of the second kind. They cited evidence, which was obtained through studies of sensitized fluorescence of mercury and cadmium vapors, to substantiate their hypothesis. The major portion of their evidence was dependent upon the intensity of a triplet emanating from the 6^3S_1 level of cadmium. This level could be excited only when 1.4 ev of energy was available in the form of relative kinetic energy between the mercury and cadmium atoms. The purpose of this research was to confirm their results and obtain some temperature versus intensity relations with the aid of improved techniques and equipment.

In the original work, the sensitized fluorescence was analyzed with the aid of a quartz spectrograph. The intensities on the spectrogram were weak and only a two point correlation was obtained between the temperatures and the intensities of the cadmium in question. One of these values of intensity was zero. In the present research, temperatures were controllable to a greater degree. The desired lines were selected for measurement by a Bausch and Lomb monochromator. A photo multiplier and D.C. amplifier system of high sensitivity were used to measure the relative intensities. This system had the advantages of speed in focusing, continuous monitoring of intensities, and a relative scale for the value of the intensities.

The problem of weak intensities again prevented the desired quantitative information from being obtained. The intensities of the triplet were less than the random fluctuations of the measuring device. Possibly this low intensity was partially due to the behavior of the materials in the absorption well. The recommended concentrations of the mercury and cadmium vapors could not be obtained under equilibrium conditions due to the pumping action of the cadmium at the optimum temperature. The addition of 2 mm. of mercury pressure of helium to the absorption cell to prevent pumping and the acquisition of a stronger mercury light source were concluded to be necessary for future experiments of this nature.