154

Spectroscopic Measurements
on
Xenon and Krypton
1953-1957

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Johns Hopkins University

λ	I_{HM}	Classification	
8987.57	200	$6p_{22}$	$6d_{22}$
9025.98	30	$6p_{11}$	$6d_{11}$
9032.18	50	$5d_{00}$	$4f_{11}$
9045.446	400	$6s_{12}$	$6p_{22}$
9096.13	50	$5d_{23}$	
9112.24	4	$5d_{23}$	
9131.59	3	$5d_{23}$	
9141.8	2	$5d_{23}$	
9152.12	20	$5d_{01}$	
9158.38	2		
9162.654	500	$6s_{11}$	$6p_{11}$
9167.52	100	$6p_{22}$	$6d_{33}$
9197.18	2	$5d_{11}$	
9203.20	30	$5d_{01}$	
9211.38	25	$5d_{01}$	
9216.51	1	$5d_{11}$	
9222.39	5	$6p_{23}$	$6d_{22}$
9245.18	3	$6p_{00}$	$8s_{11}$
9301.95	30	$5d_{34}$	
9306.64	40	$6s_{01}$	$7p_{01}$
9334.08	3	$5d_{34}$	$4f_{23}$
9374.02	10	$5d_{34}$	$4f_{44}$
9374.76	100	$5d_{34}$	$4f_{45}$
9412.01	60	$6p_{23}$	$6d_{33}$
9441.46	20	$6p_{22}$	$6d_{12}$
9442.68	20	$5d_{12}$	
9445.34	80	$5d_{12}$	$4f_{23}$
9487.76	4		
9497.07	40	$5d_{12}$	
9505.78	10	$5d_{12}$	
9513.379	200	$6p_{23}$	$6d_{34}$
9585.14	20	$6p_{22}$	$6d_{01}$
9605.80	3		
9614.43	1		
9616.95	1		
9668.94	1		
9685.32	150	$6p_{12}$	$6d_{23}$
9700.99	20	$6p_{23}$	$6d_{12}$
9710.03	2	$5d_{22}$	$8p_{22}$
9718.16	100	$6p_{11}$	$6d_{22}$

The two lower curves — June 7th 54.

M. Shekaekera S.J.

$\lambda = 2k + \delta$

FILTER 2434

III

PLANE GRATING

k: Counter reading

λ: wavelength in A.U. II Order

δ = Correction factor.

$\lambda = k + \delta$

II

FILTER 4305

I

PLANE GRATING.

k = Counter reading

λ = wavelength in A.U. I order.

δ = Correction factor

$\lambda = 2k + \delta$.

FILTER 3384

1.13.53.

λ in A°U.

359-14L KEUFFEL & ESSER CO. Millimeters, 5 mm. lines accented, cm. lines heavy. MADE IN U.S.A.

Zeiss Dr. H.C.
Pencil hard TD 24

ENGRAVING 334-3, [illegible] TO THE HALF INCH.
WHEN ORDERING STATE COLOR, DRAWING OR TRACING PAPER.
MADE IN U.S.A.
100% RAG PAPER

Grating #97.
Single Mirror (Concave).

~~ft 3305~~
2434 feller
quartz lamp at 31.84 amps.

7000 71 72 73 74 7500 7600 7700 7800 7900 8000 81 82 83 84 8500 86 87 88 89 9000

-2.74 1.31 -2.48 1.31 -2.48 1.31
-2.50 1.33 -2.76 1.59
-2.50 1.33
-2.78 1.61
-2.52 1.35
-2.80 1.63
-2.54 1.37
-2.82 1.65
-2.56 1.39
-2.84 1.67
-2.58 1.41
-2.86 1.69
-2.60 1.43
-2.88 1.71
-2.62 1.45
-2.90 1.73
-2.64 1.47
-2.92 1.75
-2.66 1.49
-2.94 1.77
-2.68 1.51
-2.96 1.79
-2.70 1.53
-2.98 1.81
-2.72 1.55
-3.00 1.83
-3.02 1.85
-3.04 1.87
-3.06 1.89
-3.08 1.91
-3.10 1.93
-3.12 1.95
-3.14 1.97
-3.16 1.99
-3.18 2.01
-3.20 2.03
-3.22 2.05
-3.24 2.07
-3.26 2.09
-3.28 2.11
-3.30 2.13
2.15
12.16

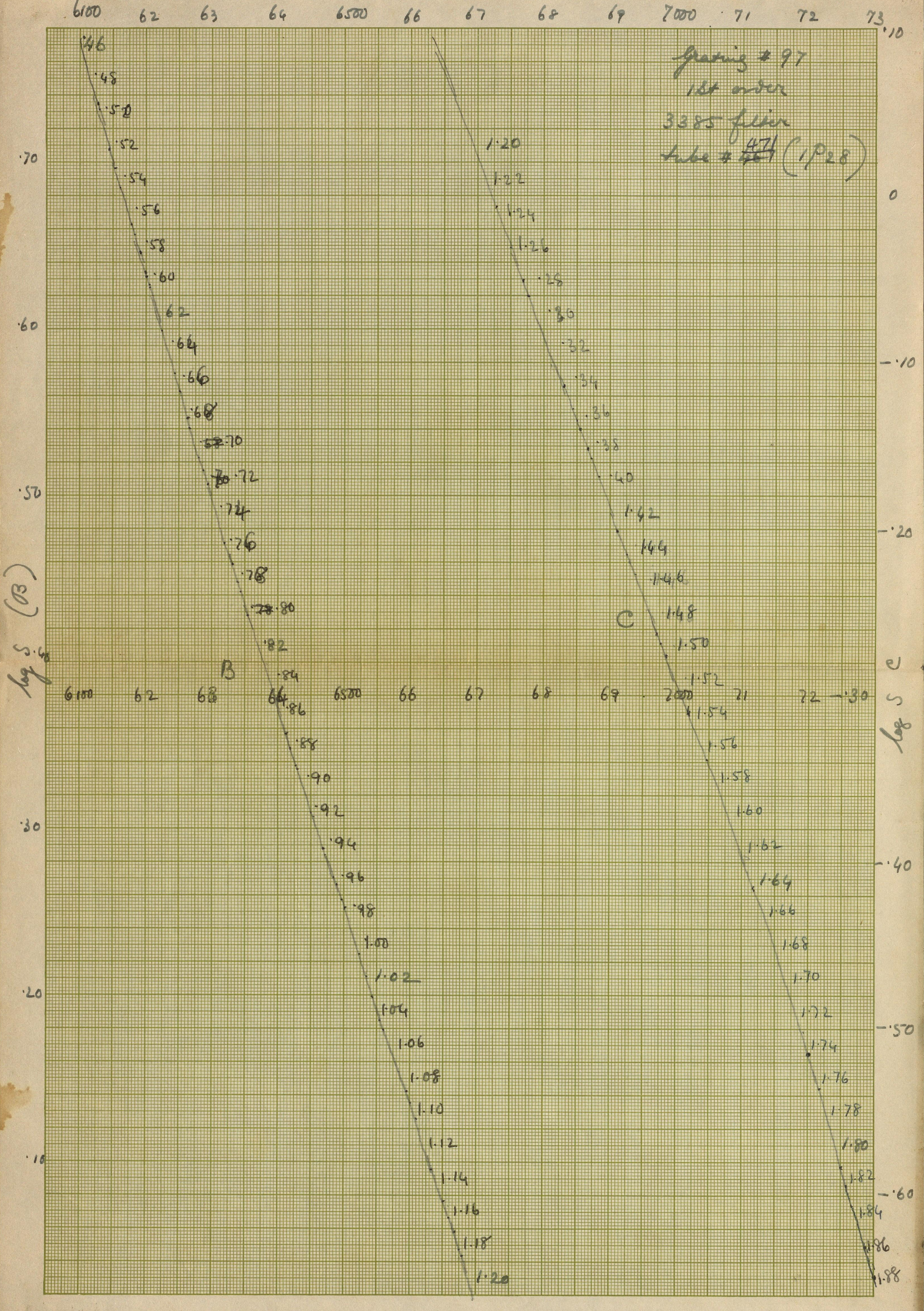
~~9000 91 92 93 94 95 96 97 98 99~~

9000 91 92 93 94 9500 96 97 98 99

.60 .50 .40 .30 .20 .10 0 -.10 -.20

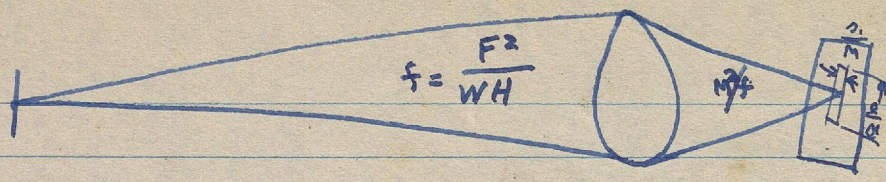
KEUFFEL & ESSER CO. N.Y.

358-14L KEUFFEL & ESSER CO.
Millimeters, 5 mm. lines accented, cm. lines heavy.
MADE IN U. S. A.



$\frac{d}{dr}\left(\frac{4}{3}\pi r^3\right) = 4\pi r^2 = A$

$\frac{A}{r^2} = 4\pi$



$\frac{\text{ergs/sec}}{\text{cm}^2}$ for 2π attending

$E_\lambda d\lambda \cdot \frac{M^2 dA}{2\pi f} \frac{\text{ergs/sec}}{\text{cm}^2}$

$E_\lambda d\lambda \cdot \frac{M^2 dA}{2\pi f} \cdot \frac{s_1}{M} \cdot \frac{l}{M}$ ergs/sec $= s_1 \cdot l \cdot \frac{WH}{2\pi F^2} \cdot E_\lambda d\lambda$ ergs/sec

What is $d\lambda$? For every small area of entrance slit, s_1, energy will be spread over exit slit s_2. In grating equation

$$\lambda = \frac{d}{n}[\sin\alpha + \sin\beta]$$

take incident angle α as fixed and let $d\beta$ represent $\frac{s_2}{F}$ the angle subtended by the exit slit. Then

$$d\lambda = \frac{d}{n}\cos\beta\, d\beta$$

$$= \frac{d}{n}\cos\beta \cdot \frac{s_2}{F}$$

Gives $S \cdot \frac{s_1 l WH}{2\pi F^2} E_\lambda \left(\frac{d}{n} \cdot \frac{s_2}{F} \cos\beta\right)$ ergs/sec through exit slit.

For line source with intensity I ergs/sec/cm² for 2π steradians energy through entrance slit is

$$I \cdot \frac{M^2}{2\pi} \cdot \frac{WH}{F^2} \cdot \frac{s_1}{M} \cdot \frac{l}{M} \text{ ergs/sec}$$

$$= \frac{s_1 l}{2\pi} \frac{WH}{F^2} \cdot I \text{ ergs/sec}$$

If exit slit is wide enough to accept whole line energy through exit slit will be

$$S \cdot \frac{s_1 l}{2\pi} \frac{WH}{F^2} \cdot I \text{ ergs/sec}$$

If s_2 is smaller than magnified s_1 must be modified by factor s_2/s_1'. For given λ $d\lambda = 0$ $d\alpha = \frac{s_1}{F}$ $d\beta = \frac{s_1'}{F}$

$$0 = \cos\alpha\, d\alpha + \cos\beta\, d\beta$$

or $$s_1' = -\frac{\cos\alpha}{\cos\beta} s_1 .$$

The neg. sign may be ignored; factor is

$$\frac{s_2}{s_1'} = \frac{s_2}{s_1} \frac{\cos\beta}{\cos\alpha}$$

Energy through exit slit is

$$S \cdot \frac{s_1 l}{2\pi} \frac{WH}{F^2} I \qquad s_2 \gg s_1'$$

or $$S \cdot \frac{s_2 l}{2\pi} \frac{WH}{F^2} \frac{\cos\beta}{\cos\alpha} \cdot I \qquad s_2 \ll s_1'$$

Relative signals:

$$\frac{i_\ell}{i_c} = \frac{S \cdot \frac{s_1 \ell}{2\pi} \frac{WH}{F^2} I}{S \cdot \frac{s_1 \ell}{2\pi} \frac{WH}{F^2} E_\lambda\left(\frac{d}{n} \frac{s_2}{F} \cos\beta\right)} =$$

$$\therefore I = \frac{i_\ell}{i_c} \cdot E_\lambda\left(\frac{d}{n} \frac{s_2}{F} \cos\beta\right) \qquad s_2 \geq s_1'$$

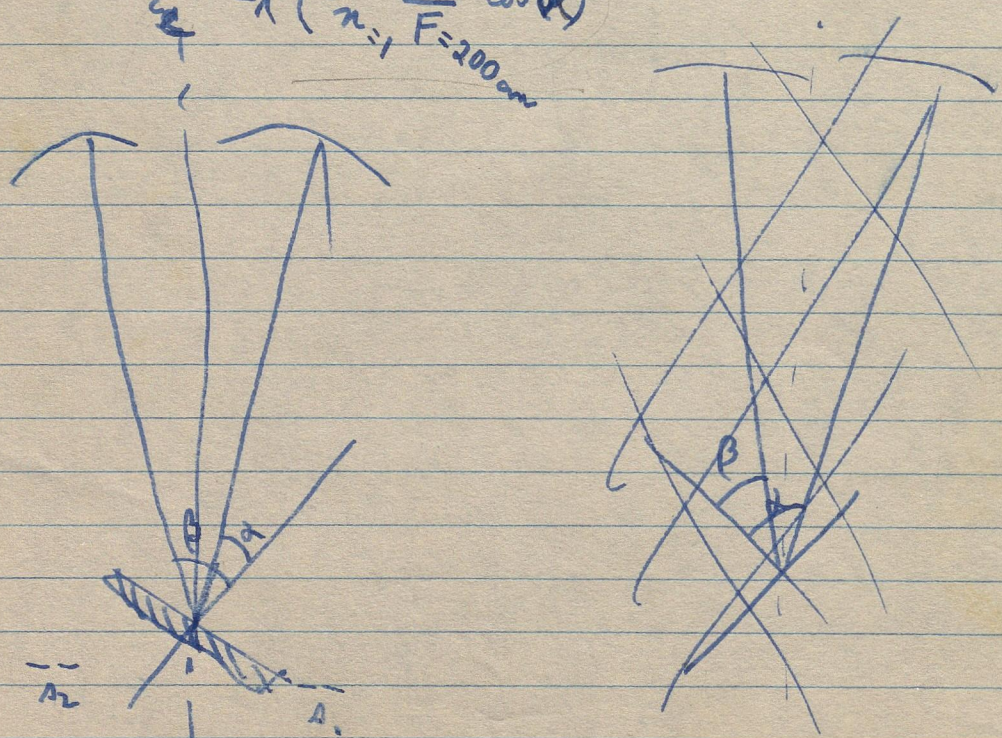
OR

$$\frac{i_\ell}{i_c} = \frac{S \cdot \frac{s_2 \ell}{2\pi} \frac{WH}{F^2} \frac{\cos\beta}{\cos\alpha} I}{S \cdot \frac{s_1 \ell}{2\pi} \frac{WH}{F^2} E_\lambda\left(\frac{d}{n} \frac{s_2}{F} \cos\beta\right)}$$

$$I = \frac{i_\ell}{i_c} \cdot E_\lambda\left(\frac{d}{n} \frac{s_1'}{F} \cos\alpha\right) \qquad s_2 \leq s_1'$$

$d = 3.3\mu = .07\text{cm}$, $n = 1$, $F = 200\text{cm}$

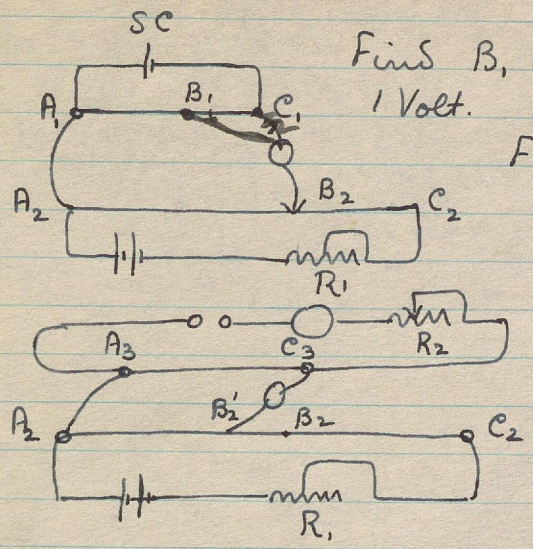
$\frac{2.54}{15{,}000} \left(= 1.67\,\mu\right)$



For $\alpha < \beta$ $\frac{\cos\alpha}{\cos\beta} > 1$ and there is magnification of entrance slit. Use $s_1 > s_2$
As variation not as large as $\cos\beta$. Large slit easier to measure.

Data Sheet 15a

POWER SUPPLY FOR TUNGSTEN LAMP.



Find B_1 on $A_1 C_1$ such that p.d. on $A_1 B_1$ is 1 Volt.

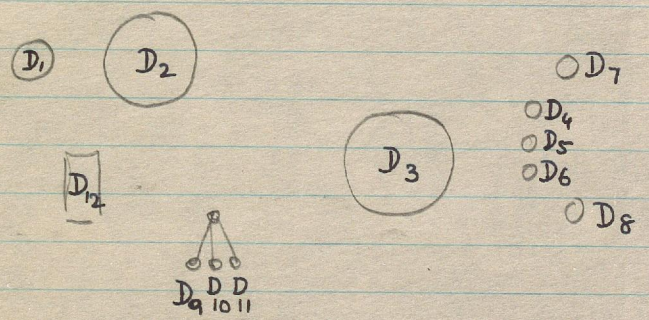
Find ~~B_2~~ R so that when dial on $A_2 C_2$ is set at 1 Volt balance is obtained. Fall of potential on $A_2 B_2$ is 1 Volt.

Find B_2' on $A_2 C_2$ so that $A_2 B_2' / A_2 B_2 = .762$

Potential fall on $A_2 B_2'$ is .762 Volt.

Connect lamp, ~~man~~ R_2 & ~~wire~~ strip $A_3 C_3$ in series. Adjust R_2 till balance is obtained.

Potential fall on $A_3 C_3$ is ∴ .762 Volt.
But resistance of $A_3 C_3$ is .01 ohm
∴ Current through $A_3 C_3$ = 76.2 amps.



D_1 to adjust so that voltage ~~fo~~ drop on $A_1 B_1$ is 1 Volt. (Turn the knob to the voltage of the standard cell).

$D_4 - D_8$ to adjust R_2 so that the battery gives voltage drop of 1 Volt on the resistances $D_2 D_3$.

$D_2 D_3$ to adjust so that segment of $D_2 D_3$ ($A_2 B_2'$) has voltage drop required by the current.

(D)
Dial on the top of the panel - to adjust current in lamp so that voltage drop on the .01 ohm is one hundredth of that on $A_2 B_2'$.

Precaution: When switching on the current see that D is set at maximum!

1·2, 7, 16

Data sheet 15 b

Lamp at 2800°K has R_{max} $(2.8)^5 \times 1.2958 \times 10^7$ ergs.

$= 223.010 \times 10^7$ ergs.

~~$\frac{R_\lambda}{R_{\lambda max}}$ for~~ $\lambda T = 2800 \times 5400 \times 10^{-8} = .1512$

$\frac{R_\lambda}{R_{\lambda max}}$ for λT .150 is .26384 | $\frac{R_\lambda}{R_{\lambda max}}$ for λT .1512 is .27371

λT .155 is .30497

$\therefore R_\lambda = .27371 \times 223.010 \times 10^7 = 61.0401 \times 10^7$ ergs.

Emissivity of tungsten at 5400Å and 2800°K = .444

$R_\lambda \cdot \varepsilon_w$ is energy emitted by the lamp at 5400Å, 2800°K

$= 27.1012 \times 10^7$ ergs.

$\frac{R_\lambda \cdot \varepsilon_w}{R_{\lambda max}} = \frac{27.1012}{223.010} = .12152$

To find the emissivity of tungsten at temperatures 3200, 3400, 3600

ε_w at 4670Å 2500°K is .462
3200°K is .452 } slope is $\frac{.010}{700}$

at 6650Å 2500 K is .425
3200 K .411 } slope is $\frac{.014}{700}$

Slope at 5400Å is $\frac{.0115}{700} = \frac{.0016}{100}$

At 5400Å ~~→~~ 2800°K ε_w = .444
3000°K " = .441
3200 .438
3400 .434
3600 .431

Choose temperature 3400°K.

R_{max} for 3400°K is $3.4^5 \times 1.2958 \times 10^7 = 588.55 \times 10^7$ ergs.

$\lambda T = 3400 \times 5400 \times 10^{-8} = .1836$

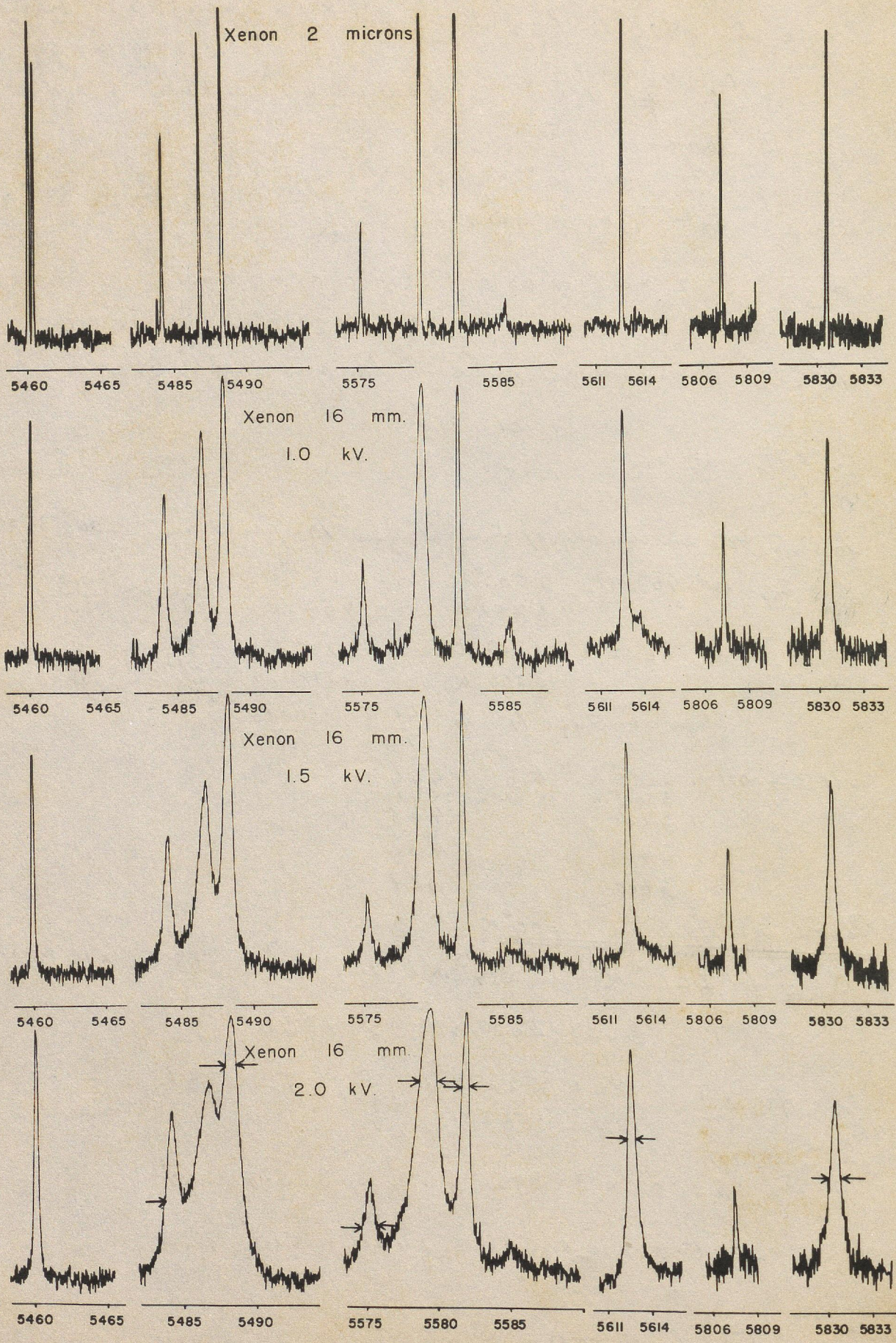
$\frac{R_\lambda}{R_{\lambda max}}$ for λT .180 = .52298
.185 = .56581 } for λT .1836, $\frac{R_\lambda}{R_{max}} = .55382$

At 3400°K ~~→~~ 5400Å

$R_\lambda = .55382 \times 588.55 \times 10^7 = 325.95 \times 10^7$

$R_\lambda \cdot \varepsilon_w = 325.95 \times 10^7 \times .434 = 141.46 \times 10^7$

$\frac{(R_\lambda \cdot \varepsilon_w)_{3400}}{(R_\lambda \cdot \varepsilon_w)_{2800}}$ for 5400Å is 5.22.


Xenon 2 microns
5460 5465 5485 5490 5575 5585 5611 5614 5806 5809 5830 5833
Xenon 16 mm.
1.0 kV.
5460 5465 5485 5490 5575 5585 5611 5614 5806 5809 5830 5833
Xenon 16 mm.
1.5 kV.
5460 5465 5485 5490 5575 5585 5611 5614 5806 5809 5830 5833
Xenon 16 mm.
2.0 kV.
5460 5465 5485 5490 5575 5580 5585 5611 5614 5806 5809 5830 5833

Data sheet 15 C.

Choose temp 3200

R_{max} for 3200°K is $3.2^5 \times 1.2958 \times 10^7 = 434.77 \times 10^7$ ergs.

$\lambda T = 3200 \times 5400 \times 10^{-8} = .1728$

$\frac{R_\lambda}{R_{\lambda max}}$ for λT .170 .43526 λT .1728, $\frac{R_\lambda}{R_{\lambda max}} = .45993$
.175 .47933

$R_\lambda = .45933 \times 434.77 \times 10^7 = 199.70 \times 10^7$

$\varepsilon_w = .438$

$\therefore R_\lambda \cdot \varepsilon_w = 87.469$

$\therefore \frac{R_\lambda}{R_{\lambda max}} = 87.469$

$\frac{(R_\lambda \cdot \varepsilon_w)_{3200}}{(R_\lambda \cdot \varepsilon_w)_{2800}} = 3.23$

Choose temp 3250 R_{max} for 3250 is $3.25^5 \times 1.2958 \times 10^7$
$= 469.79 \times 10^7$

$\lambda T = 3250 \times 5400 \times 10^{-8}$
$= .1755$

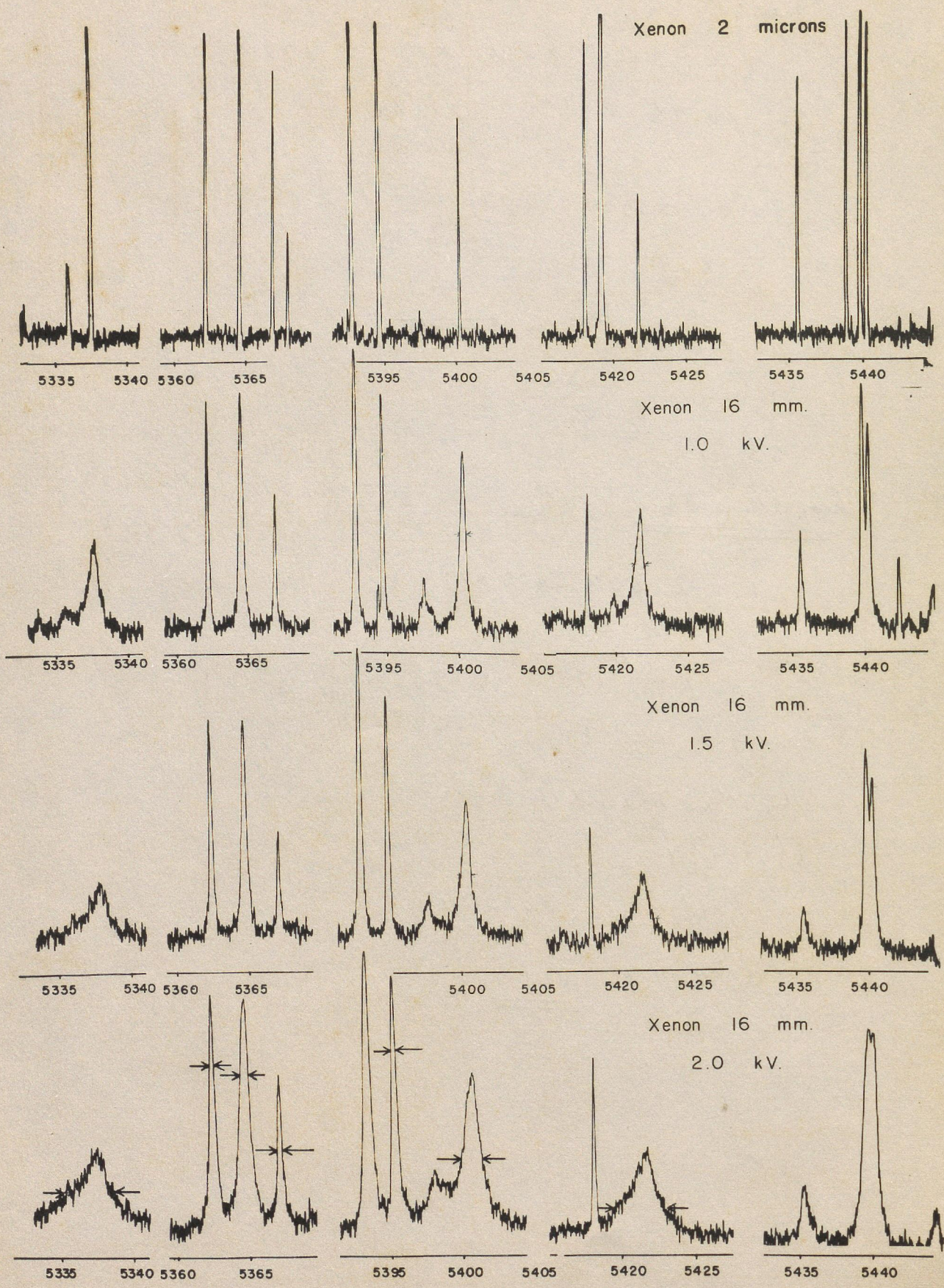
$\frac{R_\lambda}{R_{\lambda max}}$ for λT .175 .47933 for λT .1755 $\frac{R_\lambda}{R_{\lambda max}} = .48370$
.180 .52298

$\therefore R_\lambda = 227.24 \times 10^7$ ergs.

$\varepsilon_w = .437$

$\therefore R_\lambda \cdot \varepsilon_w = 99.304$

$\therefore \frac{(R_\lambda \cdot \varepsilon_w)_{3250}}{(R_\lambda \cdot \varepsilon_w)_{2800}} = 3.66$


Xenon 2 microns
5335
5340
5360
5365
5395
5400
5405
5420
5425
5435
5440
Xenon 16 mm.
1.0 kV.
Xenon 16 mm.
1.5 kV.
Xenon 16 mm.
2.0 kV.

Data sheet 16.

Constants of the function $\left\{\frac{R_\lambda}{R_{\lambda max}} R_{\lambda max} \varepsilon_w T_q \frac{d}{n} \cdot \frac{s_1}{f} \cdot \cos\alpha\right\} = F$

$R_{\lambda max}$ at $T = 1000^\circ K$ for blackbody radiation is given to be 1.2958×10^7 ergs cm^{-2} sec^{-1} μ^{-1}

$\left(\frac{R_{\lambda max}}{T^5} =\right)$ is a constant. Hence $R_{\lambda max}$ for a blackbody at $2350^\circ K$ is $1.2958 \times (2.35)^5 \times 10^7$

$R_{\lambda max} = 9.287 \times 10^8$ $\quad T_q = 4.925$. (transmission coeffᵗ of quartz.)

Filter		
4305	3900 to 5000	λ 3900 to 5000
3389	2250 to 3500	λ 4500 to 7000.

$d = 3.3$ microns. $\quad s_1 = .035$ Cm. $\quad f = 200$ Cm.

$d = 3.27$ microns.

$R_{\lambda max} \cdot T_q \cdot \frac{d}{n} \cdot \frac{s_1}{f} = 9.287 \times 10^8 \times .925 \times \frac{3.3}{1} \times \frac{.035}{200}$ for λ 4500 to 7000

$= 9.287 \times 10^8 \times .925 \times \frac{3.3}{2} \times \frac{.035}{200}$ for λ 3900 to 5000

i.e $\quad = 4.96101 \times 10^5$ for λ 4500 to 7000

$= 2.9805 \times 10^5$ for λ 3900 to 5000.

$n\lambda = d(\sin\alpha + \sin\beta)$ where α & β are angles which incident & diffracted beams make with grating normal.

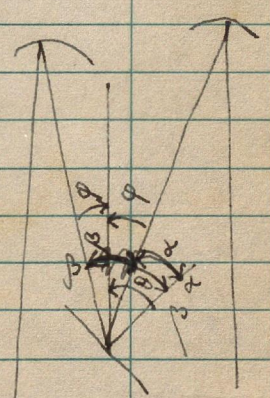
$\alpha = \theta - \varphi$ $\quad \beta = \theta + \varphi$ where φ is ∠ bet. spectrograph axis and axial ray from the mirror, θ is ∠ bet. spectrograph axis and grating normal.

$n\lambda = d \sin(\theta - \varphi) + \sin(\theta + \varphi) = \{2d \cos\varphi\} \sin\theta$.

The grating is one ruled by Dr. Strong, 14400 lines to the inch, 6" wide

$\varphi = 2.92^\circ$ $\quad d = \frac{2.54}{1.7639} \frac{2.59}{14,400} = 1.7639 \times 10^{-4}$ Cm

$\cos\varphi = .9987$



Data Sheet 16 — Calibration Curve for log F — Visible & ultraviolet

Calculation of Cos α.

λ	F = 1 − Cos α (2nd order)	Mean difference δ	Cos α calculated	Cos α (with δ)	$\left(\frac{R_\lambda}{R_{max}} \varepsilon_\omega \cos\alpha\right)$	$\left(R_{max} \tau_\beta \frac{d}{n} \frac{\delta_\lambda}{F}\right)$	$\left\{\frac{R_\lambda}{R_{max}} \varepsilon_\omega \tau_\beta \frac{d}{n} \frac{\delta_\lambda}{F}\right\}$	$\log_{10}\left\{\frac{R_\lambda}{R_{max}} \varepsilon_\omega \tau_\beta \frac{d}{n} \frac{\delta_\lambda}{F} \cos\alpha\right\}$	L calculated	Difference
3574	204	62	9796	·9858	1.2367×10^{-3}	2.9805×10^{-5}	3.6860×10^{-2}	2.5665	2.680	−114
3617	209	62	9791	·9853	1.4081		4.1968	2.6229	2.720	−097
3660	214	62	9786	·9848	1.6295		4.8567	2.6863	2.760	−074
3702	219	63	9781	·9844	1.8607		5.5458	2.7440	2.799	−055
3745	224	63	9776	·9839	2.1144		6.3020	2.7994	2.839	−040
3787	229	63	9771	·9834	2.3942		7.1315	2.8532	2.878	−025
3830	234	63	9766	·9829	2.7045		8.0608	2.9064	2.918	−012
3872	239	63	9761	·9824	3.0416		9.0655	2.9574	2.9574	+0
3915	244	62	9756	·9818	3.4095		1.0162×10^{-2}	3.0069	2.997	·010
3957	249	61	9751	·9812	3.8140		1.1368	3.0557	3.027	29
4000	253	61	9747	·9808	4.2503		1.2668	3.1027	3.077	26
4043	258	61	9742	·9803	4.7271		1.4089	3.1488	3.117	30
4085	263	61	9737	·9798	5.2373		1.5610	3.1934	3.156	37
4128	268	61	9732	·9793	5.7870		1.7248	3.2367	3.196	41
4170	273	60	9727	·9787	6.3833		1.9025	3.2793	3.235	43
4213	278	59	9722	·9781	7.0159		2.0910	3.3203	3.275	45
4256	283	59	9717	·9776	7.7018		2.2955	3.3609	3.315	46
4468	308	54	9692	·9746	1.1819×10^{-2}		3.5227	3.5468	3.572	35
4681	332	47	9668	·9715	1.7235		5.1369	3.7107	3.7107	0
4894	357	38	9643	·9681	2.4049		7.1678	3.8554	3.909	−·054
5706	387	27	9619	·9646	3.2306		9.6288	3.9836	4.106	−·122
	1st order									
4468	49	13	9951	·9964	1.2083×10^{-2}	4.9601×10^{-5}	5.9944×10^{-3}	3.7777	3.9661	−·188
4681	62	20	9938	·9958	1.7664		8.7641	3.9427	4.0502	−·107
4894	74	25	9926	·9951	2.4842		1.2324×10^{-2}	4.0907	4.1344	−·043
5706	86	31	9914	·9945	3.3307		1.6524	4.2181	4.2181	0
5319	98	36	9902	·9938	4.3415		2.1538	4.3332	4.3022	+·031
5532	111	40	9889	·9929	5.4967		2.7269	4.4357	4.3864	050
5745	123	44	9877	·9921	6.7856		3.3663	4.5271	4.4705	057
5957	135	48	9865	·9913	8.2000		4.0680	4.6094	4.5543	055
6170	148	51	9852	·9903	9.7015		4.8121	4.6823	4.6384	044
6383	160	54	9840	·9894	1.1290×10^{-1}		5.6010	4.7483	4.7226	026
6596	173	57	9827	·9884	1.2916		6.4076	4.8067	4.8067	0
6809	185	59	9815	·9874	1.4586		7.2361	4.8595	4.8908	−·031
7021	197	61	9803	·9864	1.6292		8.0825	4.9075	4.9746	−·061
7234	209	62	9791	·9853	1.7948		8.9040	4.9496	5.0587	−109

A graph

A graph

A graph

Addison-Wesley Press, Inc. Cambridge 42, Mass. Printed in U.S.A.

Data Sheet 17.

$\log\left\{\left(\frac{R_\lambda}{R_{\lambda max}}\right)R_{\lambda max}\varepsilon_\omega T_q \frac{d}{\infty}\frac{s_1}{f}\cos\alpha\right\}$ vs λ (Log F vs λ) $n = 2$; Temp. 2350°K. Tungsten window lamp.

λ	$\log(E)$ observed	Difference	$\log\left(\frac{R_\lambda}{R_{\lambda max}} R_{\lambda max} \varepsilon_\omega T_q \frac{d}{\infty}\frac{s_1}{f}\cos\alpha\right)$		λ			$\log\left(\frac{R_\lambda}{R_{\lambda max}} R_{\lambda max} \varepsilon_\omega T_q \frac{2}{n}\frac{s_1}{f}\cos\alpha\right)$	
3500	2·6110	-153	2·5957	2·458	4300	3·3559	45	3·3604	3·401
25	6343	-140	6203	2·494	25	3792	44	3836	423
50	6576	-137	6437	2·521	50	4025	43	4068	446
75	6808	-113	6695	568	75	4258	42	4300	468
3600	7041	-103	6938	601	4400	4490	40	4530	489
25	7274	-91	7183	636	25	4723	38	4761	570
50	7507	-80	7427	671	50	4956	36	4992	532
75	7740	-65	7675	709	75	5189	34	5223	553
3700	7972	-55	7917	742	4500	5422	30	5452	572
25	8205	-46	8159	775	25	5654	27	5681	592
50	8438	-38	8400	806	50	5887	23	5910	612
75	8671	-28	8643	839	75	6120	19	6139	631
3800	8904	-20	8884	870	4600	3·6353	14	6367	1649
25	9136	-12	9124	902	25	6586	10	6596	669
50	9369	-7	9362	930	50	6818	6	6824	690
75	9602	-1	9601	959	75	7057	2	7053	707
3900	9835	+6	9841	987	4700	7284	-3	7281	725
25	3·0068	11	3·0079	3·018	25	7517	-10	7507	742
50	0300	17	0317	047	50	7749	-17	7732	758
75	0533	21	0554	074	75	7982	-24	7958	774
4000	0766	25	0781	102	4800	8215	-30	8185	792
25	0999	28	1027	128	25	8448	-36	8412	809
50	1231	31	1262	154	50	8681	-42	8639	826
75	1464	35	1499	181	75	8913	-48	8865	843
4100	1697	37	1734	207	4900	9146	-56	9090	859
25	1930	40	1970	233	25	9379	-63	9316	875
50	2163	42	2205	258	50	9612	-71	9541	890
75	2395	43	2438	283	75	9845	-80	9765	905
4200	2628	44	2672	307	5000	4·0077	-89	9988	919
25	2861	46	2907	332	25	0310	-96	4·0214	935
50	3094	46	3140	355	50	0543	-104	0439	950
75	3327	46	3373	379	75	0776	-111	0665	967

Subtract ·004 from all log F values.

Form 104-H Addison-Wesley Press, Inc., Cambridge 42, Mass. Printed in U.S.A.

$\eta = 1$. Subtract .004 from all log F values

λ	log F (Calculated)	δ	log F		λ	log F (Calculated)	δ	log F.
4400	3.939	~~+94~~			6000	4.571	54	4.625
50	959	−194	3.765		50	591	52	.643
4500	979	174	805		100	611	48	.659
50	998	154	844		50	631	45	.676
4600	4.018	137	881		200	650	41	.691
50	038	118	920		50	670	37	.707
4700	058	102	956		300	690	33	.723
50	077	84	993		50	710	29	.739
4800	097	67	4.030		400	729	24	.753
50	117	54	063		50	749	18	.767
4900	137	42	095					
50	156	31	125		6500	769	+13	.782
					50	789	+ 6	.795
5000	176	−20	156		600	808	0	.808
50	196	− 10	186		50	828	−7	.821
5100	216	− 1	215		700	848	−14	.834
50	235	+ 8	243		50	868	−22	.846
5200	255	+15	270		800	887	−29	.858
50	275	+~~8~~23	298		50	907	−36	.871
300	295	+ 29	324		900	927	43	.884
350	314	34	348		50	947	50	.897
400	334	~~39~~	371					
450	354	43	397		7000	966	58	.908
					50	986	68	.920
5500	374	47	421		100	5.006	78	.928
50	~~393~~	51	444		50	026	90	.936
600	413	53	466		200	045	101	.944
50	433	55	488		50	065	113	.953
700	453	56	509		300	085	−127	.958
50	473	57	530					
800	492	57	549					
50	512	57	569					
900	532	56	588					
950	555	56	611					

Form 104-H Addison-Wesley Press, Inc., Cambridge 42, Mass. Printed in U.S.A.

Data Sheet 18

$$F = \left\{ \left(\frac{R_\lambda}{R_{\lambda max}} \right) R_{\lambda max} \cdot E_w \cdot T_q \cdot \frac{d}{n} \cdot \frac{\delta_1}{f} \cdot \cos\alpha \right\}$$

$\delta_1 \& \delta = .035$ cm $T_q = .925$

$n = 2$ for λ 3500 to 5075 $\quad d = 3.3$ microns

$n = 1$ for λ 4450 to 7300.

$\frac{R_\lambda}{R_{\lambda max}}$, E_w, $\cos\alpha$ variables.

$R_{\lambda max} = 9.287 \times 10^8$ ergs cm^{-2} sec^{-1} μ^{-1}

ULTRAVIOLET

λ	log(F)	λ	log(F)
3500	2·458	4300	3·401
25	2·494	25	3·423
50	2·521	50	3·446
75	2·568	75	3·468
3600	2·601	4400	3·489
25	2·636	25	3·570
50	2·671	50	3·532
75	2·709	75	3·553
3700	2·742	4500	3·572
25	2·775	25	3·592
50	2·806	50	3·612
75	2·839	75	3·631
3800	2·870	4600	3·649
25	2·902	25	3·669
50	2·930	50	3·690
75	2·959	75	3·707
3900	·987	4700	3·725
25	3·018	25	3·742
50	3·047	50	3·758
75	3·074	75	3·774
4000	3·102	4800	3·792
25	3·128	25	3·809
50	3·154	50	3·826
75	3·181	75	3·843
4100	3·207	4900	3·859
25	3·233	25	3·875
50	3·258	50	3·890
75	3·283	75	3·905
4200	3·307	5000	3·919
25	3·332	25	3·935
50	3·355	50	3·950
75	3·379	75	3·967.

VISIBLE

λ	log(F)	λ	log(F)
4400	—		
4450	3·765	6000	4·625
500	3·805	050	4·643
550	3·844	100	4·659
600	3·881	150	4·676
650	3·920	200	4·691
700	3·958	250	4·707
750	3·993	300	4·723
800	4·030	350	4·739
4800	4·030	6400	4·753
850	4·063	450	4·767
900	4·095	500	4·782
50	4·125	550	4·795
5000	4·156	600	4·808
50	4·186	650	4·821
100	4·215	700	4·834
? ~~150~~ →	(2)·243	750	4·846
5200	4·270	6800	4·858
250	4·298	850	4·871
300	4·324	900	4·884
350	4·348	950	4·897
400	4·371	7000	4·908
450	4·397	050	4·920
500	4·421	100	4·928
550	4·444	150	4·936
5600	4·466	7200	4·944
650	4·488	250	4·953
700	4·509	300	4·958.
750	4·530		
800	4·549		
850	4·569		
900	4·588		
950	4·611		

Form 104-H Addison-Wesley Press, Inc., Cambridge 42, Mass. Printed in U.S.A.

$s_1 = .07$ cm ∞ $n = 1$. $F = \left\{ \frac{R_\lambda}{R_{\lambda max}} R_{\lambda max} \tau_g \omega \cdot \frac{d}{n} \cdot \frac{s_1}{f} \cdot \cos\alpha \right\}$

INFRA-RED

λ	log F	λ	log F	λ	log F	λ	log F
5500	4.727	7000	5.203	8500	5.422	10,000	5.508
550	749	050	214	550	426	050	509
600	769	100	224	600	431	100	511
650	792	150	234	650	435	150	512
700	816	200	243	700	439	200	513
750	829	250	252	750	443	250	513
800	847	300	262	800	447	300	513
850	868	350	271	850	451	350	514
900	885	400	280	900	455	400	515
950	902	450	288	950	458	450	517
6000	4.923	7500	5.296	9000	5.462	10500	5.517.
050	941	550	305	050	466		
100	958	600	313	100	470		
150	976	650	320	150	472		
200	994	700	328	200	475		
250	5.011	750	335	250	478		
300	026	800	343	300	481		
350	039	850	350	350	484		
400	054	900	356	400	487		
450	069	950	363	450	489		
6500	5.083	8000	5.369	9500	5.490		
550	096	050	376	550	492		
600	109	100	381	600	494		
650	122	150	387	650	497		
700	134	200	392	700	499		
750	147	250	397	750	500		
800	158	300	402	800	501		
850	169	350	408	850	504		
900	180	400	412	900	507		
950	192	450	417	950	508		

Subtract .004 from all log F values

Form 104-H Addison-Wesley Press, Inc., Cambridge 42, Mass. Printed in U.S.A.

Data sheet 19. $\left(\frac{R_\lambda}{R_{\lambda max}} E_w \cos\alpha\right)$ log F for infrared region.

① T = 2350.	②	③	④	⑤	Product of ③, ④ & ⑤	$\left(R_{\lambda max} \times T_{gx} \times \frac{d}{s} \times \frac{s_1}{f}\right)$		log(F)	(mx + C)	δ
λT	λ in A.U.	$R_\lambda / R_{\lambda max}$	E_w	Cos α as Calculated on reverse						
·130	5532	12371×10^{-1}	·4475	·9929	5.4967×10^{-2}		5.4538×10^{4}	4.7367	4.879	−142
·135	5745	1.5422	·4437	·9921	6.7856		6.7327	4.8282	914	86
·140	5957	1.8800	·4397	·9912	8.2000		8.1361	4.9104	952	42
·145	6170	2.2469	·4360	·9903	9.7015		9.6259	4.9835	9835	0
·150	6383	2.6384	·4323	·9894	1.1290×10^{-1}		1.1202×10^{5}	5.0493	5.018	31
·155	6596	3.0497	·4287	·9885	1.2916		1.2815	5.1077	053	54
·160	6809	3.4759	·4250	·9874	1.4586		1.4472	5.1605	088	72
·165	7021	3.9148	·4219	·9864	1.6292		1.6165	5.2085	123	85
·170	7234	4.3526	·4185	·9853	1.7948		1.7808	5.2506	158	93
·175	7447	4.7933	·4149	·9840	1.9569×10^{-1}	9.92204×10^{5}	1.9416	5.2880	193	95
·180	7660	5.2298	·4120	·9829	2.1178		2.1013	5.3224	228	94
·185	7872	5.6581	·4089	·9816	2.2710		2.2533	5.3528	263	90
·190	8085	6.0745	·4055	·9803	2.4147		2.3959	5.3795	297	82
·195	8298	6.4762	·4020	·9789	2.5485		2.5286	5.4029	332	70
·200	8571	6.8605	·3988	·9775	2.6744		2.6536	5.4239	367	56
·205	8723	7.2252	·3954	·9761	2.7886		2.7669	5.4420	402	40
·210	8936	7.5688	·3922	·9745	2.8928		2.8702	5.4579	437	21
·215	9149	7.8900	·3889	·9730	2.9856		2.9623	5.4716	472	0
·220	9362	8.1879	·3856	·9715	3.0673		3.0434	5.4833	506	−23
·225	9574	8.4619	·3823	·9698	3.1373		3.1128	5.4932	541	−48
·230	9787	8.7117	·3790	·9681	3.1964		3.1715	5.5013	576	−75
·235	10000	8.9375	·3760	·9664	3.2476		3.2223	5.5082	611	−103
·240	10213	9.1394	·3726	·9646	3.2848		3.2592	5.5131	646	−133
·245	10426	9.3179	·3692	·9627	3.3119		3.2861	5.5167	681	−164
·250	10638	9.4735								
·255	10851	9.6071								
·260	11064	9.7193								
·265	11276	9.8112								
·270	11489	9.8837								
·275	11702	9.9377								
·280	11914	9.9744								
·285	12128	9.9948								

$\log F = (mx + C) + \delta$

where $m = \frac{\log F_2 - \log F_1}{\lambda_2 - \lambda_1}$; ~~$x = \log F - \log F_1$~~

$C = \log F_1$ & $x = \lambda - \lambda_1$.

$\lambda_1 = 6170$ $\lambda_2 = 9362$.

δ graph

Calculations for Cos α

From data on data sheet 15

	f = 1 - Cos α Calculated	Difference	f actual	Cos α
5532	111	40	71	
5745	123	44	79	
5957	135	47	88	
6170	148	51	97	
6383	160	54	106	
6596	172	57	115	
6809	185	59	126	
7021	197	61	136	
7234	209	62	147	
7447	222	62	160	
7660	234	63	171	
7872	246	62	184	
8085	258	61	197	
8298	271	60	211	
8511	283	58	225	
8723	295	56	239	
8936	308	53	255	
9149	320	50	270	
9362	332	47	285	
9574	345	43	302	
9787	357	38	319	
10000	369	33	336	
10213	381	27	354	
10426	394	21	373	

Values entered on reverse.

$R_\lambda max = 9.28704 \times 10^8$ ergs cm^{-2} sec^{-1} μ^{-1}

$T_q = .925$

$d = 3.3$ microns

$n = 1.$

$\delta_1 = .07$ cm.

$f = 200$ cm.

$R_\lambda max \cdot T_q \cdot \frac{d}{n} \cdot \frac{\delta_1}{f}$

$= 9.28704 \times 10^8 \times .925 \times \frac{3.3}{1} \times \frac{.07}{200}$

$= 9.92204 \times 10^5$

~~$\frac{1.9979 \times 10^5}{2989} = 67066295 \times 10^{-4}$~~

~~$\frac{1.9997 \times 10^5}{2979} = 67126525$~~

$\frac{4881}{2979} = 1638469284$

Data sheet 20.

Subtract .006 from all log F values

$F = \frac{R_\lambda}{R_{\lambda max}} \cdot R_{\lambda max} \cdot \varepsilon_w \cdot \tau_g \cdot \frac{d}{n} \cdot \frac{s_1}{f}$

$s_1 = .07$ Cm.

$n = 1.1.$

temp 2350

	log(F) calculated		log(F)				log(F)
5500	4.874	-147	4.727	7250	5.160	92	.252
50	882	-133	749	300	.169	93	.262
600	890	-121	769	350	.177	94	.271
650	898	-106	792	400	185	95	.280
700	906	95	816	450	193	95	.288
750	915	86	829				
800	923	76	847	7500	201	95	.296
850	931	63	868	550	210	95	.305
900	939	54	885	600	218	95	.313
950	947	45	902	650	226	94	.320
				700	234	94	.328
6000	956	33	923	750	242	93	.335
050	964	23	941	800	251	92	.343
100	972	14	958	850	259	91	.350
150	980	− 4	976	900	267	89	.356
200	988	+ 6	994	950	275	88	.363
250	997	14	5.011				
300	5.005	21	.026	8000	283	86	.369
350	013	26	.039	050	292	84	.376
400	021	33	.054	100	299	82	.381
450	029	40	.069	150	308	79	.387
		45		200	316	76	.392
6500	038	45	.083	250	324	73	.397
550	046	50	.096	300	332	70	.402
600	054	55	.109	350	341	67	.408
650	062	60	.122	400	349	63	.412
700	070	64	.134	450	357	60	.417
750	079	68	.147	500	- 8 -	- -	
800	087	71	.158	8500	365	57	.422
850	095	74	.169	550	373	53	.426
900	103	77	.180	600	382	49	.431
950	111	81	.192	650	390	45	.435
				700	398	41	.439
7000	119	84	.203	750	406	37	.443
050	128	86	.214	800	414	33	.447
100	136	88	.224	850	423	28	.451
150	144	90	.234	900	431	24	.455
200	152	91	.243	950	439	19	.458

9000	5·447	+15	5·462						
050	455	11	466						
100	464	6	470						
150	472	0	472						
200	480	−5	475						
250	488	−10	478						
300	496	−15	481						
350	505	−21	484						
400	513	−26	487						
450	521	−32	489						
		-							
9500	529	−39	490						
550	537	−45	492						
600	545	−51	494						
650	554	−57	497						
700	562	−63	499						
750	570	−70	500						
800	578	−76	501						
850	586	−82	504						
900	595	−88	507						
950	603	−95	508						
10,000	611	−103	508						
050	619	110	509						
100	627	116	511						
150	636	124	512						
200	644	131	513						
250	652	139	513						
300	660	147	513						
350	668	154	514						
400	677	162	515						
450	685	168	517						
10500	693	176	517						

Form 104-H Addison-Wesley Press, Inc., Cambridge 42, Mass. Printed in U.S.A.

Dispersion Correction.

$\boxed{\lambda \text{ vs. } \alpha}$

Let $\delta = 1 - \cos\alpha$; δ is an increasing function of α and hence of λ

$$\frac{\delta - \delta_0}{\delta_1 - \delta_0} = \frac{\alpha - \alpha_0}{\alpha_1 - \alpha_0} \quad \frac{\lambda - \lambda_0}{\lambda_1 - \lambda_0}$$

$$\therefore \delta = \delta_0 + \left\{\frac{\delta_1 - \delta_0}{\lambda_1 - \lambda_0}\right\} \lambda - \lambda_0.$$

The variation of $\delta_{(calculated)}$ from δ_{actual} is plotted against wavelength

λ vs $\cos\alpha$

$(\delta_{calculated} \sim \delta_{actual}) \propto \lambda^2$

$\lambda \propto \alpha$

γ

$\cos\alpha$

First order

Second order

3500 4000 4500 5000

4000 5000 6000 7000 8000 9000 10,000 11000

λ

.99 .98 .97 .96 .95

18 16 14 12 10 8 6

.0050 .0040 .0030 .0020 .0010 0

355-141 · KEUFFEL & ESSER CO.
Millimeters, 5 mm. lines accented every cm. lines heavy
MADE IN U.S.A.

Graph 1

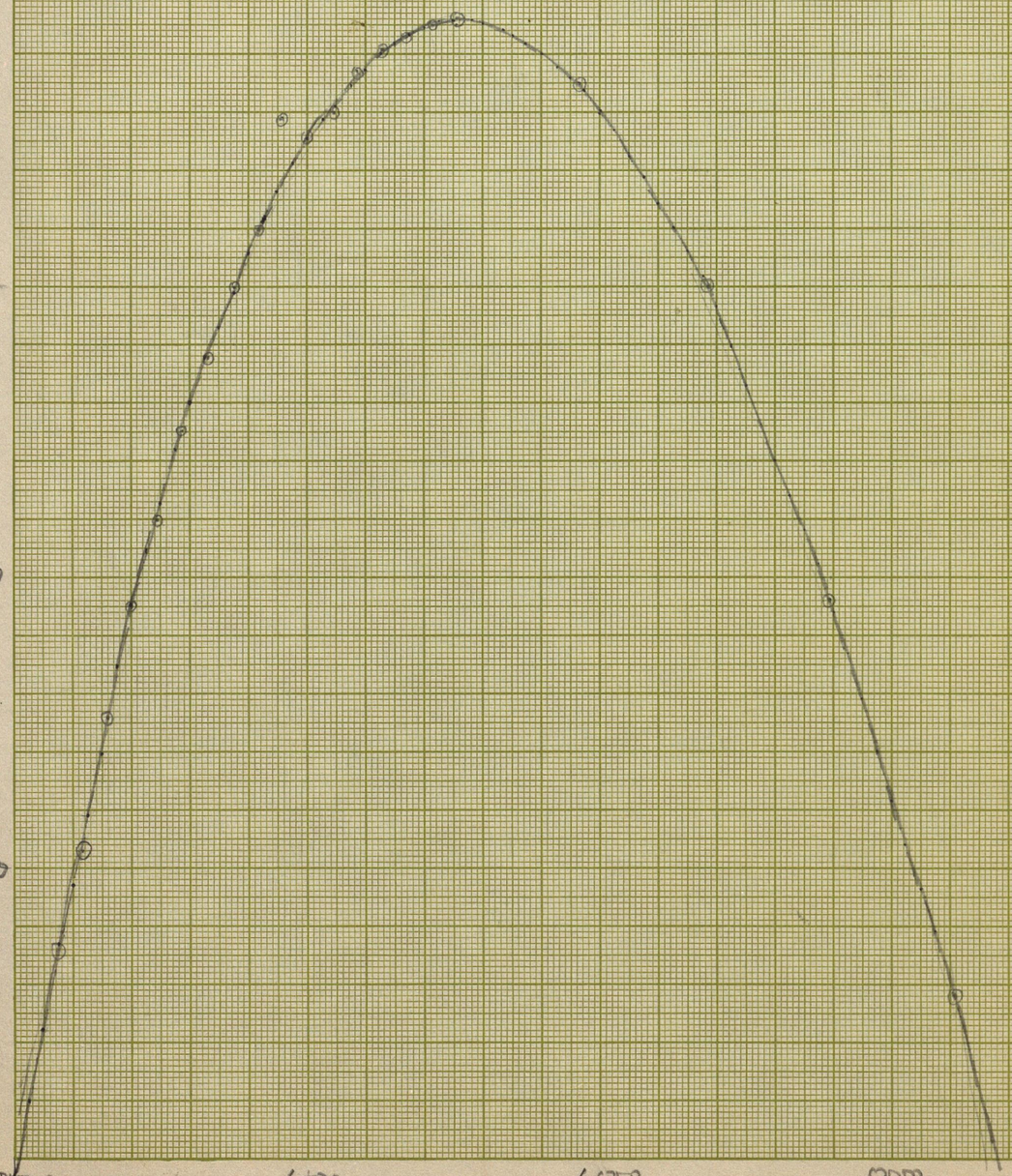
Data sheet 16

Curves for $\cos \alpha$

Difference δ vs. λ

cf Data sheet 16.

H. Thekaekara VJ.



358-14L KEUFFEL & ESSER CO.
Millimeters, 5 mm. lines accented, cm. lines heavy.
MADE IN U. S. A.

Graph 2

Calibration Curve for log F.

Data sheet 16

Difference δ vs λ

Cf data sheet 16

50

0

-50

-100

150

4000 4500 5000 5300 6000 6500 7000 7500

359-14L KEUFFEL & ESSER CO.
Millimeters, 5 mm. lines accented, cm. lines heavy.
MADE IN U. S. A.

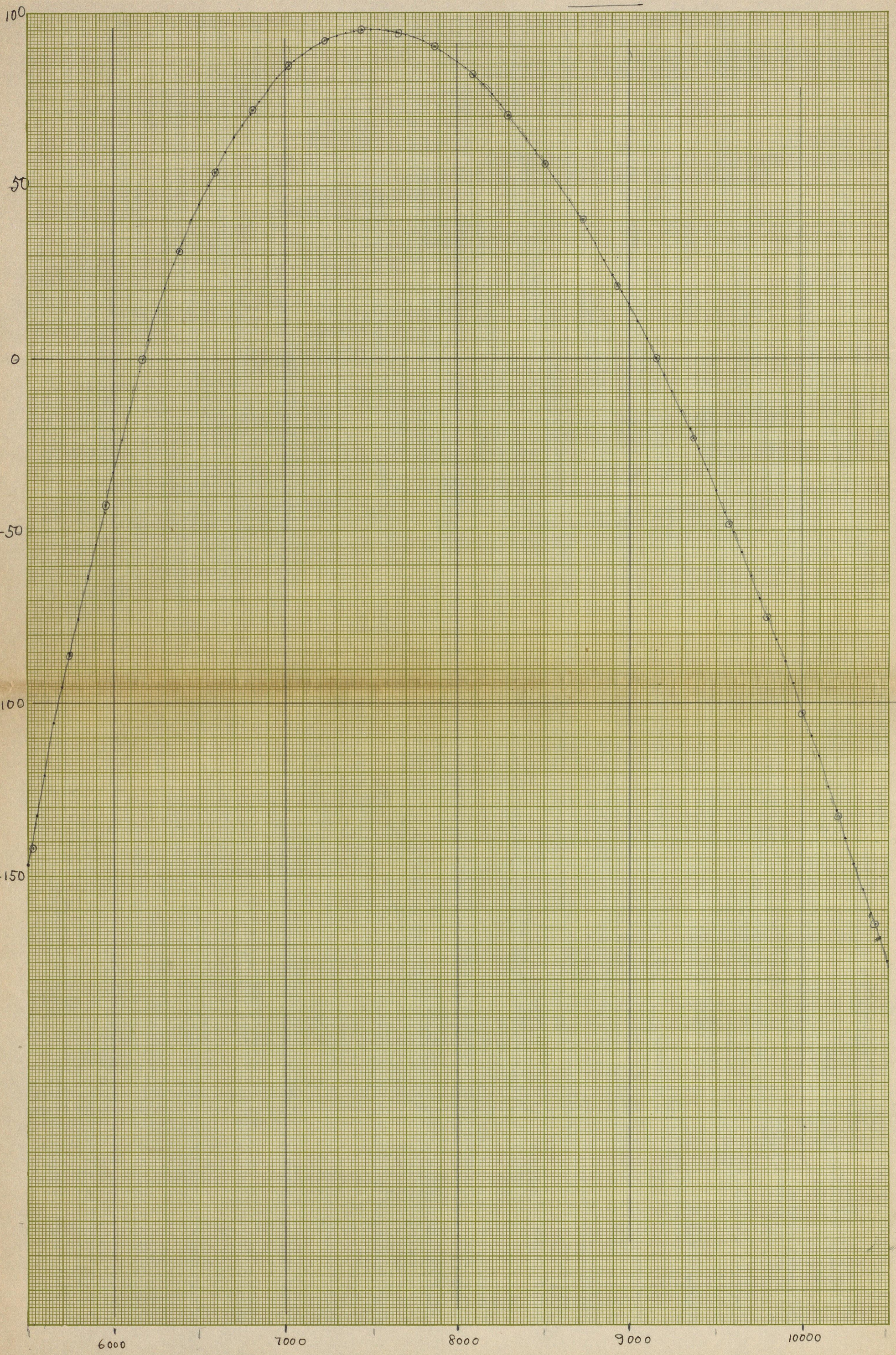
Graph 3

Calibration Curve for log F.

Data sheet 16

358-14L KEUFFEL & ESSER CO.
Millimeters, 5 mm. lines accented, cm. lines heavy.
MADE IN U. S. A.

δ vs λ



Graph 4.

Calibration Curve for
log F

Data sheet 19

358-14L KEUFFEL & ESSER CO.
Millimeters, 5 mm. lines accented, cm. lines heavy.
MADE IN U. S. A.

λ ~~Microns~~ A.U.

5600 5700 5800 5900 6000 6100 6200 6300 6400 6500 6600 6700 6800

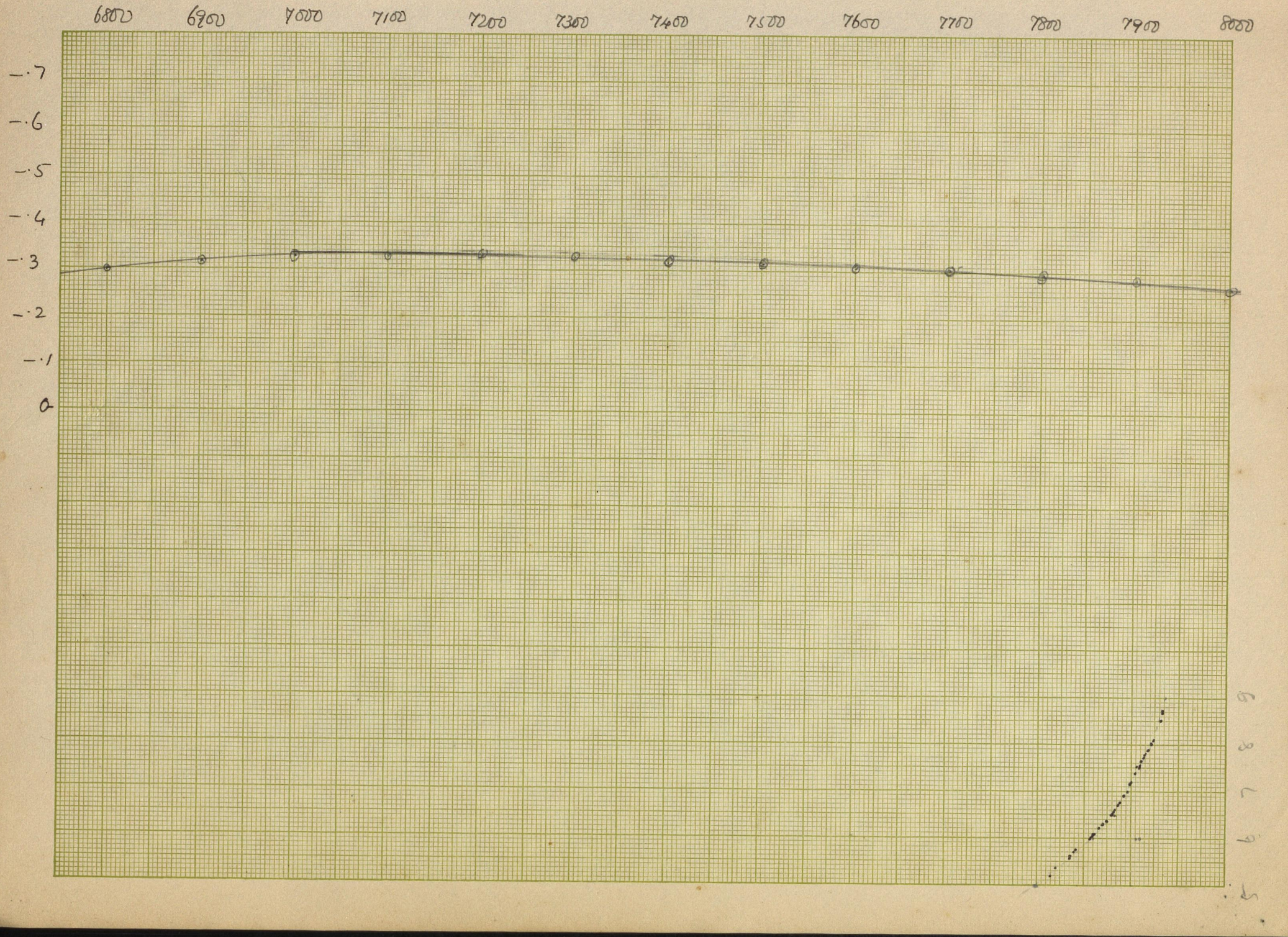
−·8 −·7 −·6 −·5 −·4 −·3 −·2 −·1 0 ·1 ·2 ·3 ·4 ·5 ·6 ·7 ·8 ·9 1·00 1·1 1·2 1·3 1·4 1·5 1·6 1·7 1·8 1·9 2·00 2·1 2·2 2·3 2·4 2·5 2·6 2·7 2·8 2·9 3·00

Filter 2434.

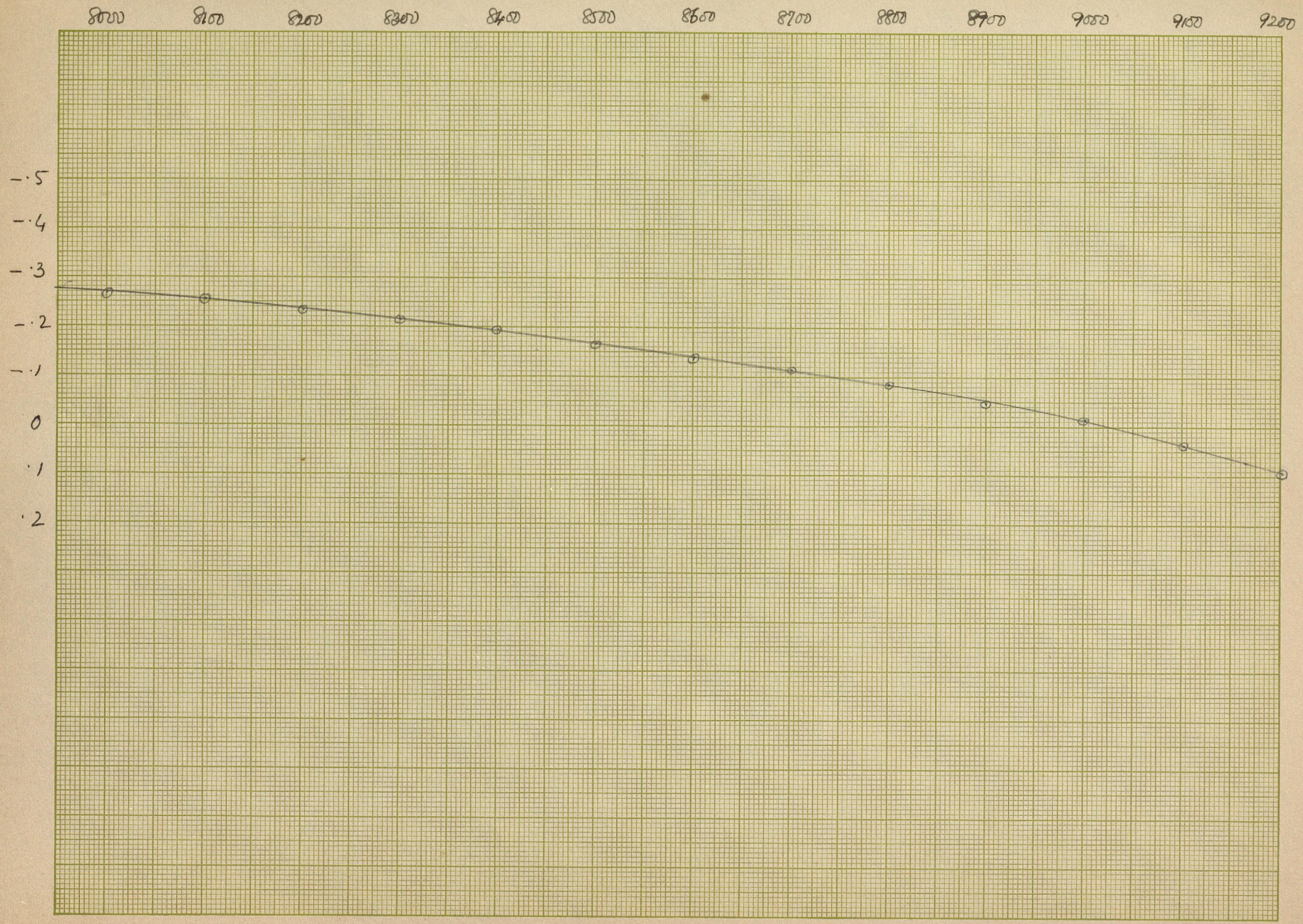
Data sheet 15.

M. Hakkarainen S.J.

358-14 KEUFFEL & ESSER CO.
Millimeters, 5 mm. lines accented, cm. lines heavy.
MADE IN U.S.A.



358-14 KEUFFEL & ESSER CO.
Millimeters, 5 mm. lines accented, cm. lines heavy.
MADE IN U.S.A.



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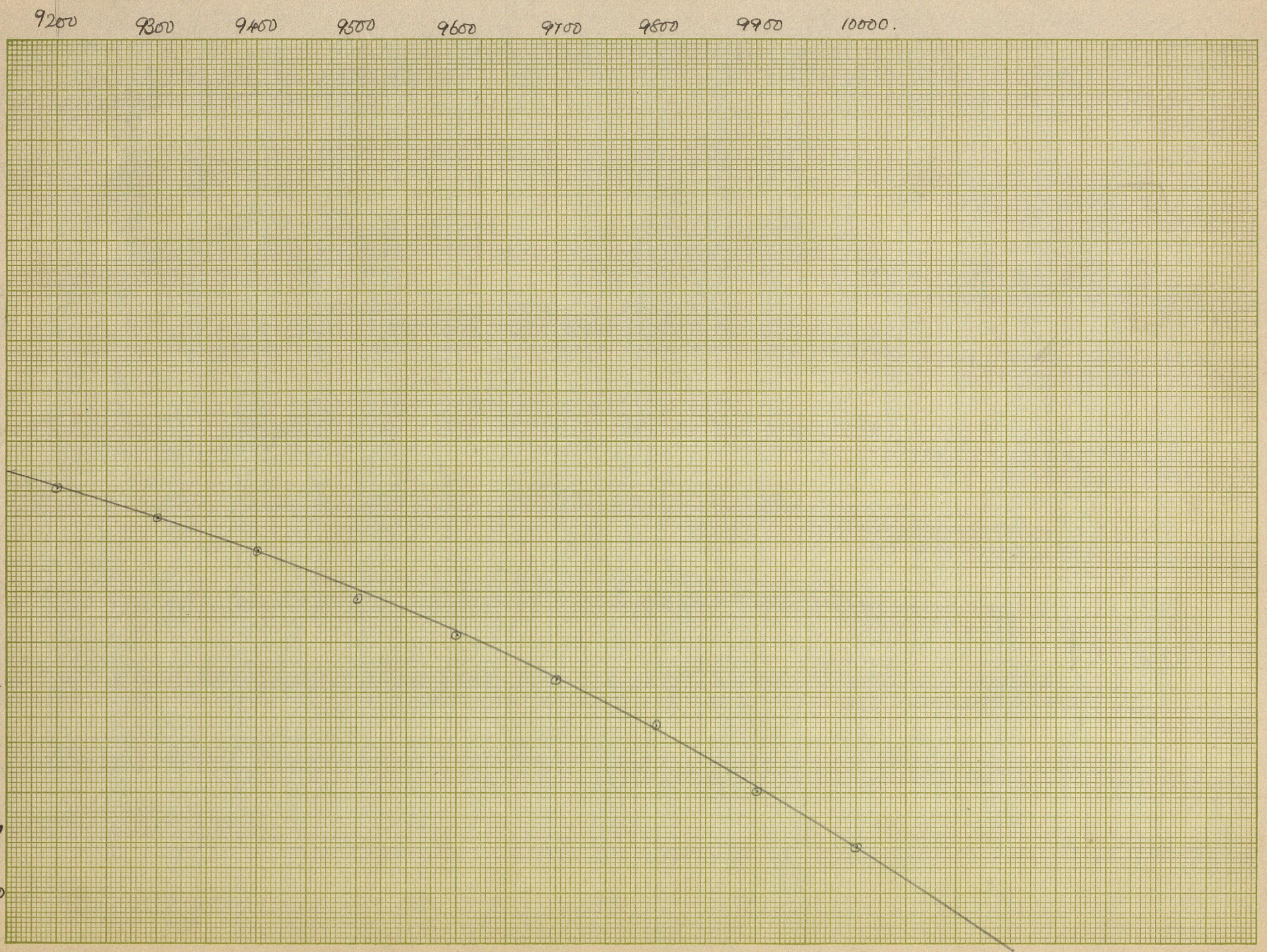
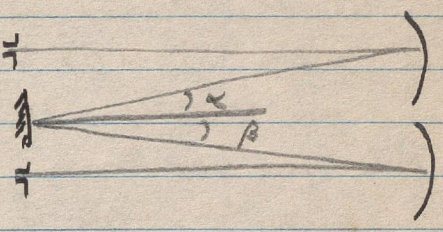
Millimeters, 5 mm. lines accented, cm. lines heavy.
MADE IN U.S.A.



Note on Dependence of intensity on the width of the lines

I order $(\sin\alpha + \sin\beta) = N\lambda$

where $N = \frac{15000}{2.56} = 5859$ lines per inch



$\alpha \simeq \beta$

$\therefore \sin\alpha = \frac{N\lambda}{2}$

λ	$\sin\alpha$	α	$\cos\alpha$	$n = \frac{\cos\alpha}{f.N.\times 10^{-8}\times 10}$
5000 A.U	·145	8°	·99	8·5 A.U per mm.
7500	·22	13°	·97	8·3
10,000	·29	17°	·96	8·2

Let β change to $\beta + d\beta$ while α is constant. $\cos\beta\, d\beta = N\, d\lambda$

$d\beta = \frac{N d\lambda}{\cos\beta}$ $dx = f.d\beta$ where f. focal length of the mirror = 200 cms.

$\therefore dx$ the linear separation of two Spectral lines differing by 1 A.U. $= f.\frac{N\times 10^{-8}}{\cos\beta}$

$\therefore$ Number of A.U. per mm $= \frac{\cos\beta}{200} \cdot \frac{\cos\beta}{f.N.\times 10^{-8}\times 10} = n$

II order $\sin\alpha = N\lambda$

λ	$\sin\alpha$	α	$\cos\alpha$	n
4000	·23	13°	·97	4·2
5000	·29	17°	·96	4·1

$\cos\beta\, d\beta = 2N d\lambda$ $\therefore dx = \frac{f.2N.10^{-8}}{\cos\beta}$

$n = \frac{\cos\beta}{f.2N.10^{-8}\times 10}$

Slit width is ·35 mm for 4000 to 5000 II order.

Hence 1·5 A.U per width of slit

Slit width is ·35 mm for 5000 to 7000

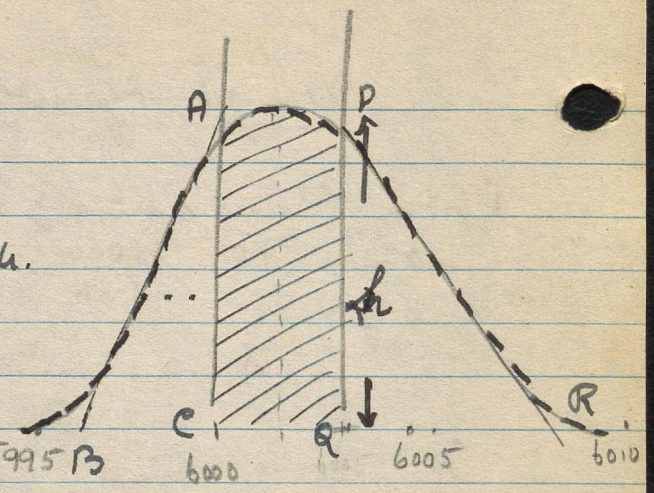
Hence 3·0 A.U per width of slit

Slit width is ·7 mm for 7000 to 10,000

Hence 6.0 A.U. per width of slit

PTO

Suppose the contour of the line as seen by the Paschen is as in figure
Slit width is .07 m.m.
Hence on the Paschen Plate at 6000 A.U.
(500 A.U. for 400 Cm/m) .07 m.m
corresponds to .09 A.U.
Hence the line contour is very closely what is observed on the plate.



Assume the intensity is measured as $\log I = 2.3$ or $I = 200$ on the plane grating (.35 m.m slit)
$200 = 3h$ the area of the shaded portion.
Area of $\Delta ABC = 1.5h$
Area of $\Delta PQR = 2h$
Actual area $= 6.5h = 433$

Corrected value of intensity is ~~2.63~~ 433 ; $\log I = 2.63$

Photo-electric measurement of intensity

Xenon.

The basic equation used in the computation is

$$\frac{I_\ell}{i_\ell} = \frac{F}{i_c} = S \quad \text{where} \quad F = \left(\frac{R_\lambda}{R_{\lambda max}}\right) R_{\lambda max} \cdot \tau_q \cdot \varepsilon_w \cdot \frac{d}{n} \cdot \frac{\delta}{f} \cdot \cos\alpha.$$

P.T.O

I_ℓ is the intensity of the line in ergs cm^{-2} sec^{-1} μ^{-1}
i_ℓ & i_c are signal strengths with the line source and standard source.

The table gives values of log I_ℓ for four conditions of xenon discharge:

(1), (2) & (3) electrode less discharge, 2350 Mc/s Raytheon, V shaped antenna, 100% power and (4) glow discharge, 40 ma current.

The pressure of the gas is

1) $\approx$ 2 μ, the vapour pressure of xenon at liquid N_2 temp.
2) .07 mm, the pressure at which the intensity is a maximum
3) 16 mm the pressure at which the tube was filled initially.
4) 4.1 mm pressure near which the intensity shows a very flat minimum.

The value of 4.1 mm pressure was selected as best suited for glow discharge since at this pressure operation of the tube is safe, and the dependence of intensity on ~~temp~~ pressure is less critical than at any other value of pressure.

All values of i_ℓ are computed on the microamp scale of the recorder; the run for i_c was made on the same scale.

Three filters were used for regions as below:

Filter	4305	for λ	3948 to 4972
	3389		4500 to 6910
	2434		5875 to 10023.

For the overlap region 4500 to 4972 the values listed on the table are those from filter 4305 since the second order gives a greater resolution; and for the overlap region

$i_c = S.\ E_\lambda\, d\lambda$ (1) for the continuous spectrum.
S is an all inclusive factor depending on the geometry of the instrument.

$\lambda = \frac{d}{n}(\sin\alpha + \sin\beta)$ (2) $\quad d\lambda = \frac{d}{n}\cdot\cos\beta\, d\beta$ (3) ; $d\beta = \frac{S_2}{F}$ (4)

$d\lambda = \frac{d}{n}\cos\beta\frac{S_2}{F}$ (5)

$\frac{\text{Energy}}{\text{sec}} = S.\ \frac{S_1 l}{2\pi}\ \frac{WH}{F2}\ E_\lambda\, d\lambda$ (6) i.e. $\frac{\text{Energy}}{\text{sec}} = S.\ \frac{S_1 l}{2\pi}\cdot\frac{WH}{F2}\ E_\lambda\ \frac{d}{n}\cdot\frac{S_2}{F}\cos\beta$ (7)

For line source

$\frac{\text{Energy}}{\text{sec}} = S.\ \frac{S_1 l}{2\pi}\cdot\frac{WH}{F2}\cdot J.$ (9)

S' is the image of S_1 at exit ; Suppose $S_2 < S_1'$

$0 = \cos\alpha\, d\alpha + \cos\beta\, d\beta$; $d\alpha = \frac{S_1}{F}$; $d\beta = \frac{S_1'}{F}$ $\therefore \frac{S_2}{S_1'} = -\frac{S_2}{S_1}\frac{\cos\beta}{\cos\alpha}$.

For $S_2 > S_1'$ $\frac{\text{Energy}}{\text{sec}} = S.\ \frac{S_1 l}{2\pi}\ \frac{WH}{F2}\cdot J$; For $S_2 < S_1'$, $\frac{\text{Energy}}{\text{sec}} = S.\ \frac{S_2 l}{2\pi}\ \frac{WH}{F2}\cdot J$

$S_2 > S_1'$ $\quad \frac{i_l}{i_c} = \frac{E_l}{E_c} = \frac{S.\ \frac{S_1 l}{2\pi}\cdot\frac{WH}{F2}\cdot J_l}{S.\ \frac{S_1 l}{2\pi}\ \frac{WH}{F2}\cdot E_\lambda\ \frac{d}{n}\cdot\frac{S_2}{F}\cos\beta}$

$I_l = \frac{i_l}{i_c}\cdot E_\lambda\cdot\frac{d}{n}\cdot\frac{S_2}{F}\cos\beta$ $\quad$ for $S_2 > S_1'$

$I_l = \frac{i_l}{i_c}\cdot E_\lambda\cdot\frac{d}{n}\cdot\frac{S_1}{F}\cos\alpha$ $\quad$ for $S_2 < S_1'$

The sine drive

For uniform rotation of the grating $\frac{d\lambda}{dx}$ i.e. the dispersion of λ with ~~long~~ position on the chart paper is not independent of λ

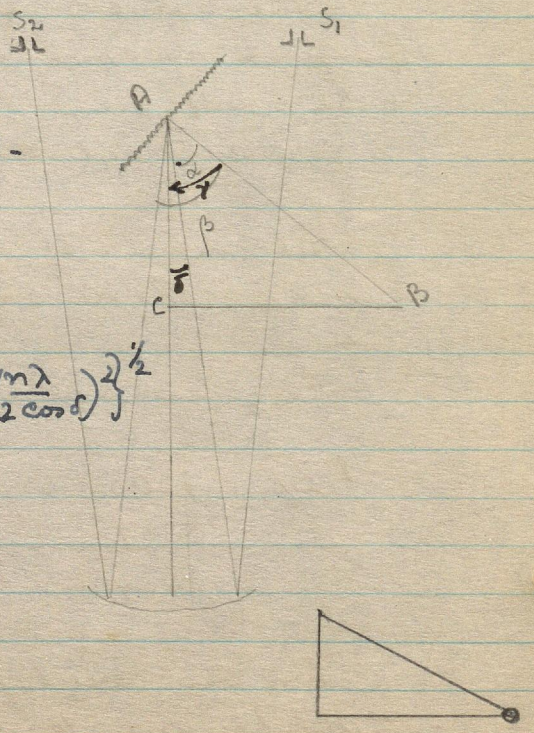
Proof $\sin(\gamma-\delta) + \sin(\gamma+\delta) = n\lambda$

i.e. $2\sin\gamma\cos\delta = n\lambda$

Since ~~dx~~ $d\gamma = c_1\, dx$, $\frac{d\lambda}{dx} = c_1\frac{2\cos\delta}{n}\left\{1-\left(\frac{n\lambda}{2\cos\delta}\right)^2\right\}^{1/2}$

i.e. as λ increases $d\lambda/dx$ decreases.

For the sine drive the end of AB rests on a glass plate carried by CB, and BC swings in the direction CB at uniform rate $\frac{dy}{dt}$.



$\frac{y}{AB} = \sin\gamma\ ;\ \frac{1}{AB}\frac{dy}{dt} = \cos\gamma\frac{d\gamma}{dt}$.

$\therefore \frac{d\lambda}{dx}$ is a constant independent of λ.

5875 to 6910 the values listed are those from filter 3389 since slit widths on this case are nearly half those for filter 2434.

In the region 3948 to 4972 eight lines were compared with records made on top of line with λ fixed, pressure varying. It was observed that while the values of i_ℓ at 2μ & 16mm were the same as those given by scanning (pressure constant, λ varying), those at .07mm were on an average 5 percent higher. The difference was fairly consistent for all lines. This shows that apparently the pressure during the scanning was slightly off the value for which intensity is maximum. In the neighbourhood of .07m the curve of intensity vs pressure has a very sharp peak and a pressure variation of .005 mm is sufficient to account for the observed difference in intensity.

Hence all computed values of log I_ℓ (filter 4305) .07mm were scaled up by .02

In the overlap region between filters 4305 & 3389, the log I_ℓ values of 3389 were seen to be lower by small amounts than those of 4305. The difference for any given pressure was fairly consistent within 4 or 5 % of the mean. This necessitated a scaling up of log I_ℓ (filter 3389) by .04 for 2μ; .11 for .07mm .06 for 16mm & .01 for glow discharge.

In the overlap region between filters 3389 and 2434 the difference for all lines was in the neighbourhood of .04 and hence all log I_ℓ values between λ6910 & λ10023 were scaled up by .08 for 2μ; .15 for .07mm; .10 for 16mm & .05 for glow discharge.

For calculation of $|V_{pn}|^2$ from intensity values.

$$I = N_p \frac{64\pi^4 e^2 \nu_{pn}^4}{3c^3} |V_{pn}|^2$$

Table of Xe II Terms.

Electron Configuration							
$5s^2 5p^5$			$^2P^\circ_1$	0	(171068·4)		
			$^2P^\circ_0$	10,537·3			
$5s5p^6$			$^2S_0$	90,873·83			
	Term limit $5s^2 5p^4\ ^3P$		Term limit $5s^2 5p^4\ ^1D$		Term limit $5s^2 5p^4\ ^1S$		
$5s^2 5p^4 6s$	$^4P_2$	93,068·4					
	$^4P_1$	95,064·34	$^2D_2$	109,563·15			
	$^4P_0$	101,157·51	$^2D_1$	112,924·70	$^2S_0$	124,070·09	
	$^2P_1$	102,799·06					
	$^2P_0$	104,250·06					
$5s^2 5p^4 6p$	$^4D^\circ_3$	113,705·33					
	$^4D^\circ_2$	113,512·29					
	$^4D^\circ_1$	116,783·11	$^2F^\circ_3$	130,064·03			
	$^4D^\circ_0$	120,414·87	$^2F^\circ_2$	128,867·19			
	$^4P^\circ_2$	111,958·84					
	$^4P^\circ_1$	111,792·08	$^2D^\circ_2$	132,207·68	$^2P^\circ_1$	140,215·22	
	$^4P^\circ_0$	113,672·85	$^2D^\circ_1$	131,913·76	$^2P^\circ_0$		
	$^4S^\circ_1$	121,628·80					
	$^2D^\circ_2$	123,112·50	$^2P^\circ_1$	129,667·37			
	$^2D^\circ_1$	124,289·50	$^2P^\circ_0$	132,741·09			
	$^2P^\circ_1$	123,254·61					
	$^2P^\circ_0$	124,571·02					
	$^2S^\circ_0$	121,179·82					
$5s^2 5p^4 5d$	$^4F_4$	99,404·90					
	$^4F_3$	98,822·86					
	$^4F_2$	101,535·65	$^2G_4$				
	$^4F_1$		$^2G_3$				
	$^4D_3$	95,437·60					
	$^4D_2$	95,396·68	$^2F_3$	114,913·96			
	$^4D_1$	96,033·44	$^2F_2$	114,751·08			

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Table of Xe II terms

Electron Configuration	Term		Term		Term	
	$5s^2 5p^4\ ^3P$		$5s^2 5p^4\ ^1D$		$5s^2 5p^4\ ^1S$	
$5s^2 5p^4 5d$	$^4D_0$	96,858.14				
	$^4P_2$	106,475.17	$^2D_2$	112,703.58	$^2D_2$	119,085.5
	$^4P_1$	107,381.75	$^2D_1$	111,326.93	$^2D_1$	124,302.18
	$^4P_0$	105,947.54				
	$^2F_3$		$^2P_1$	127,527.4		
	$^2F_2$		$^2P_0$	127,010.7		
	$^2D_2$	108,007.25				
	$^2D_1$	107,907.50	$^2S_0$	129,248.5		
	$^2P_1$	105,313.33				
	$^2P_0$	106,906.11				
$5s^2 5p^4 7s$	$^4P_2$	132,518.7				
	$^4P_1$	133,189.2	$^2D_2$	146,305.4	$^2S_0$	
	$^4P_0$	135,060.9	$^2D_1$	149,802.4		
	$^2P_1$	142,382.2				
	$^2P_0$	142.930.0				
$5s^2 5p^4 6d.$	$^4F_4$					
	$^4F_3$	136,597.7	$^2G_4$			
	$^4F_2$	139,094.1	$^2G_3$			
	$^4F_1$	139,640.3				
	$^4D_3$	135,507.2				
	$^4D_2$	135,547.0	$^2F_3$			
	$^4D_1$	135,708.2	$^2F_2$	154.032.3		
	$^4D_0$	138,726.4				
	$^4P_2$	143,399.4	$^2D_2$	149,697.3	$^2D_2$	
	$^4P_1$	144,140.2	$^2D_1$	148.085.2	$^2D_1$	
	$^4P_0$	140,883.4				
	$^2F_3$		$^2P_1$			
	$^2F_2$		$^2P_0$			
	$^2D_2$	144,385.0	$^2S_0$			
	$^2D_1$	145,940.1				
	$^2P_1$					
	$^2P_0$	145,222.7				

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Table of Xe II terms.

Unclassified even levels.

2_0	132,916·6	10_2	136,726·5
$4_{0 \text{ or } 1}$	133,454·2	12_1	138,062·8
6_2	133,915·1	14_2	146,927·8
8_2	136,569·6		

Unclassified odd levels.

1°_1	137,269·5	23°_1	143,469·8
3°_3	139,005·4	25°_1	147,518·0
5°_1	139,128·84	27°_2	147,544·6
7°_1	139,182·92	29°_1	147,568·6
9°_1	139,948·63	31°_1	148,374·9
11°_2	139,646·1	33°_1	148,952·4
13°_0	140,011·5	35°_2	149,281·0
15°_2	140,030·11	37°_2	149,682·7
17°_0	140,185·65	39°_1	156,302·9
19°_1	140,335·12	41°_1	157,222·1
21°_1	140,987·0		

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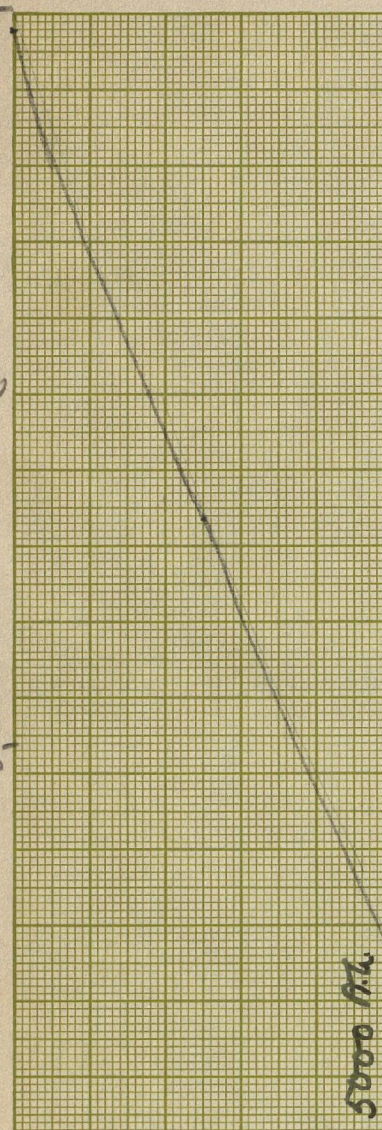

CALIBRATION CURVE I

Conversion factor $f = \frac{d\tilde{\nu}}{dx}$ in $cm^{-1}/mm.$

dx = distance bet. lines on Paschen plates. (I order) in mm.

$d\tilde{\nu}$ = shift in cm^{-1}.

Thus 1 mm separation bet. lines at 6000 A.U. = 3.65 cm^{-1} shift.

358-14L KEUFFEL & ESSER CO.
Millimeters, 5 mm. lines accented, cm. lines heavy.
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CALIBRATION CURVE II

Conversion factor $f = \frac{d\tilde{\nu}}{dx}$ in cm^{-1}/mm

dx : Distance between lines on Paschen plates (I orders) in mm.

3.5
3
2.5
2
1.5
1
.5
0

3.00 — 1000 A.U.
2.50 — 1500 A.U.
2.00 — 2000 A.U.
1.50 — 3000 A.U.

6500 7000 7500 8000 8500 9000

CALIBRATION CURVE III

Conversion factor $f = \frac{d\bar{\nu}}{dx}$ in cm^{-1}/mm

dx = distance between lines in II order Paschen plates.

III a

III b

III c

3000 A.U.

3500 A.U.

4000 A.U.

4500 A.U.

2-11-54.

2500 3000 3500 4000 4500 5000

Calibration Curves

for converting

shift in mm to shift in cm^{-1}

Edlén Sept 29, 1956.

4/22 Xenon, observed values for nf' levels.

	$n=4$	5	6	7	8
nf'_{22}	101429.8 −3595.4	103931.9 −6097.5	~~(105292.9 −7458.5)~~		
nf'_{34} nf'_{23} nf'_{33}	101425.8 −3591.1	(4.3) 103928.7 −6094.3	(3.2) 105288.7 −7454.3	106108.3 −8273.9	106639.6 −8805.2

In pure pair-coupling nf' should have zero splitting. By including the parameter G_2 in the formulae one finds that nf'_{22} should be shifted upwards by an amount equal to 5/4 of the splitting of (nf_2 of same n). The rest of the nf' levels should coincide even in this approximation.

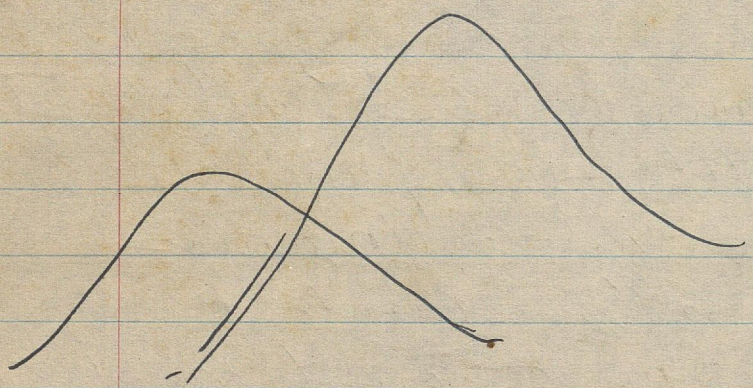
Possible identification of np' levels:

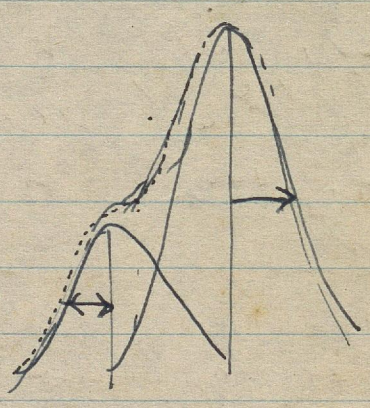
$\nu_{obs.}$	
21880	$6s'_{01} - 7p'_{12}$;
25644	$6s'_{01} - 8p'_{12}$

Shortley Phys. Rev. 44, 666 (1933)

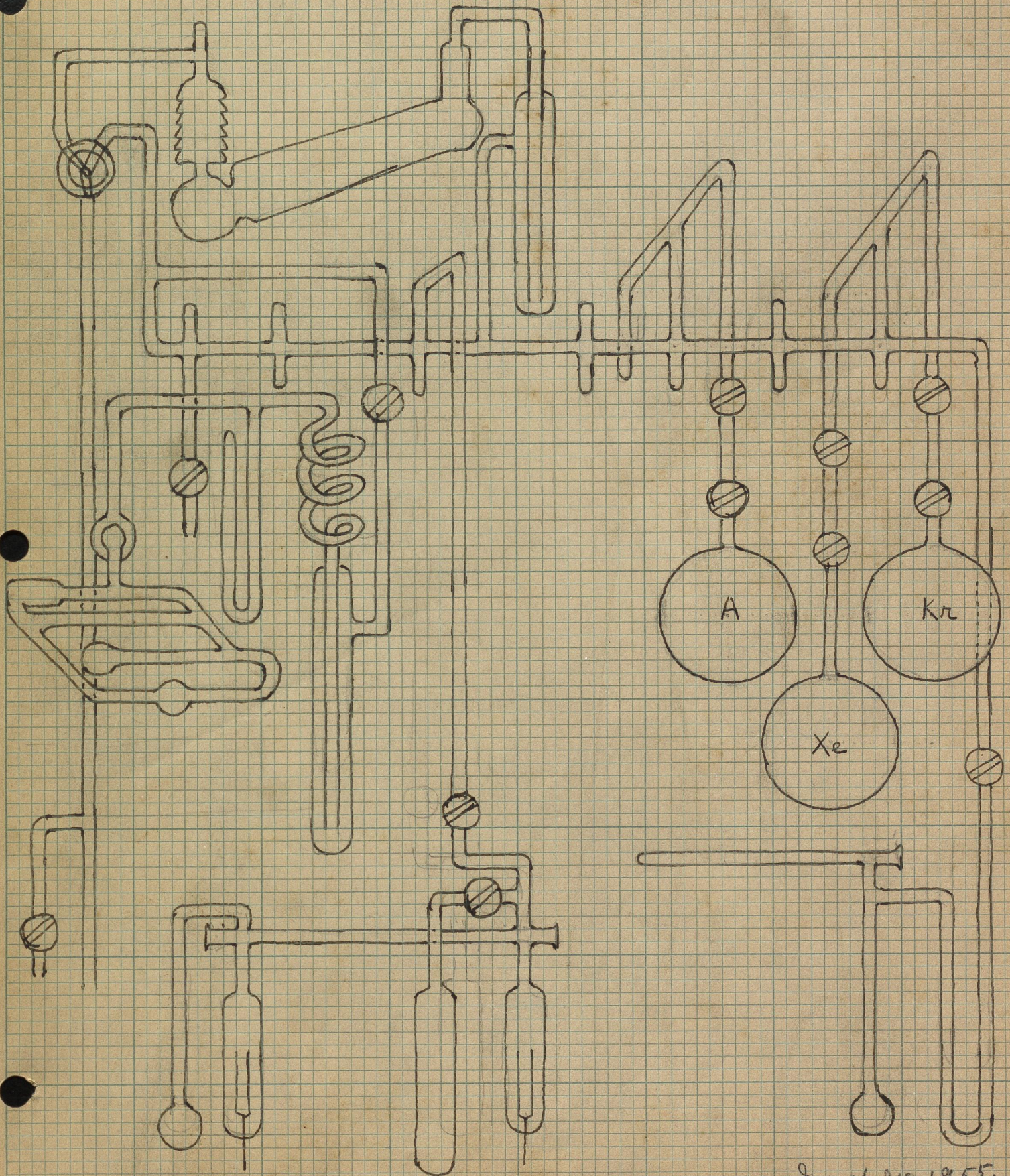
Shortley and Fries, Phys. Rev., 54, 749 (1938)

5107





K+E 353-10
10 x 10 to the inch.



March 25, 1955.

KEUFFEL & ESSER CO.
MADE IN U.S.A.

BENGT EDLÉN

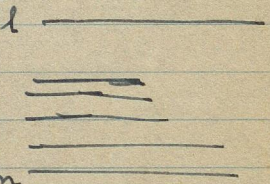
Sept 10, 1956

When we look at the tables of levels we may feel that all that is to be known about atomic spectra is already known. But it is not only details that need to be filled in. Rare earth spectra is not known. The spectra of light elements needs revision. Spectrograms reveal many unknown lines. The spectra of C & Fe IV have much left to be investigated. Fe IV is the forbidden transitions explain many lines in stars. II & III Spectra of rare gases are poorly known. Thus even term analysis is a field where work is still to be done.

Term analysis requires regularities to be established. Thus Ritz Series is one of the regularities in atomic spectra. Polarization theory for non penetrating orbits. Fine structure & its dependence on n. Different types of coupling, in particular pair coupling. Perturbed series specially in are spectra of rare gases. Some of these are well known; others are not found in literature.

Rydberg Series of levels

$$T_n = E_l - E_{n.} = \frac{R Z_0^2}{(n^*)^2}$$



R is Rydberg Const; n^* is effective quantum number. $Z_0 = 1$ for 1st spectrum $Z_0 = 2$ for 2nd Spectrum.

$n - n^* = \delta$ where δ is quantum defect.

δ is Const for Rydberg formula

$\delta = a + \beta T_n$ for Ritz formula. $= a + \frac{b}{(n^*)^2}$

$\frac{1}{(n^*)^2} = t$

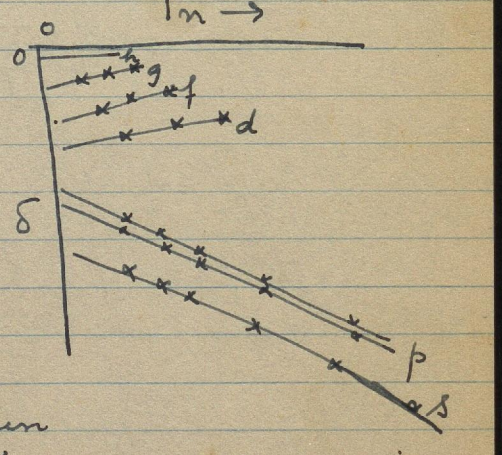
$\therefore \delta = a + bt$

These curves for δ are best studied in alkali like spectra

We take Mg II which is the best known in this type of spectra.

We expect ns, np, nd, nf, ng, nh.

ns	$^2S_{1/2}$		
np	$^2P_{1/2}$	$^2P_{3/2}$	
nd	$^2D_{3/2}$	$^2D_{5/2}$	



All these curves run smoothly for increasing n values and approach straight lines for increasing n values.

Negative slope / for non penetrating orbits

Thus a decreases with l [$l = 0$ for s; $= 1$ for p]

a is always positive

b is positive for penetrating orbits.

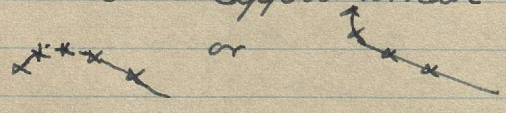
	a	b
s	1.07	.10
p	.70	.17
d	.05	−.13
f	.004	−.02
g	.0002	−.006
h		

~~I've noticed that~~

(1) The natural way of improving on the Ritz eqn is $\delta = a + bt + ct^2 + dt^3 \ldots$

Four terms express the term values within an accuracy of .02 cm^{-1}.

Here we assume that we know the limit exactly.

How to get E_l : Assume approximate E_l ; the curve will be  or

Change E_l till we get a smooth curve approaching the series limit.

(2) Non penetrating orbits : They have been treated theoretically. Departures of energy from the hydrogenic value can be accounted for by the polarization of the atomic core.

The core gets an electric dipole due to the electron.

The energy $-\frac{1}{2}\alpha\frac{e^2}{r^4}$ where αF is the dipole

Putting in the wave mechanical value of $\langle r^4 \rangle$ we get

$$T - T_0 = \alpha \frac{R Z_0^4}{a_0^3} \frac{3n^2 - l(l+1)}{2n^5 (l-\frac{1}{2}) l (l+\frac{1}{2}) (l+1)(l+\frac{3}{2})}$$ where T_0 is hydrogenic $\frac{R Z_0^2}{n^2}$

a_0 = Bohr radius

Thus if the energy depression is exclusively due to this effect, $T - T_0$ is known in terms of one adjustable parameter

$T - T_0 = A\, p(n,l)$ where A is a parameter to be empirically determined.

In Mg II, determining A from the g series

$A = 859860\ cm^{-1}$

$l = 4$; $ng\,^2G$ gives $T - T_0 = 248.14\,(3n^2 - 20)/n^5$

$l = 5$ $nh\,^2H$ $T - T_0 = 89.08\,(3n^2 - 30)/n^5$

These equations to $T - T_0 = A\, p(n,l)$ are valid for p to h series so that checks the polarization theory.
~~Thus~~
This can be extrapolated for higher l values.
In this sense the spectrum of Mg II is completely known.

Would the expression hold for f, d, ...
With f series quadrupole polarization has to be considered.

$$T - T_0 = A\, p(n,l) + B\, q(n,l)$$

q is an expression for quadrupole polarizability known from theory.
A & B are calculated from two terms for which have sufficiently high $T - T_0$.

If the core is not that of a rare gas, thus in a two electron system resonance effects come in
This ~~exp~~ procedure is valid only for one electron system.

(3) Doublet Separation $^2P_{1/2}$ $^2P_{3/2}$ in Mg II.

n	ΔT	$\Delta n^* \times 10^5$
3	91.6	121.2
4	30.5	123.4
5	13.8	124.4
6	7.4	125
7	4.41	1.26
8	2.54	126
9	1.93	126

The value of Δn^* is constant.

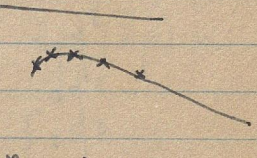
$\Delta T \propto \Delta n^* / (n^*)^3$

$\therefore \Delta T \propto (n^*)^{-3}$ since $\zeta_{nl} \propto \frac{1}{n^{*3}}$

$\Delta T = \frac{3}{2} \zeta_p$ where ζ is spin orbit interaction parameter.

Sept 18, '56 Note to (1)

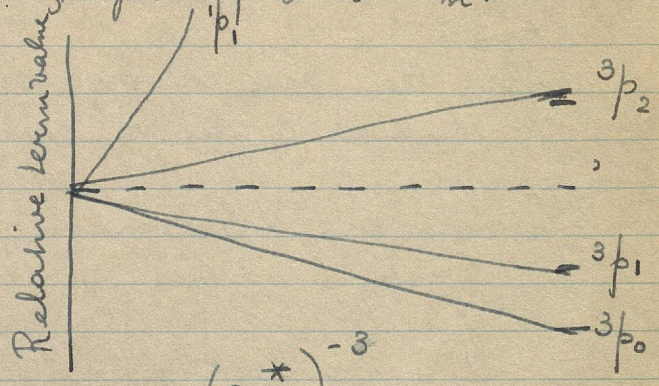
The eqn $\delta = a + bt + ct^2 + dt^3$ is valid only as long as the atom is unperturbed. In the case of Na the higher term were shown seen to deviate from the straight line.



(4) Structure of the terms of Rydberg series of in case of atoms with more than one electron.

$S\,^2S\; np \begin{cases} {}^1P_1 \\ {}^3P_2 \\ {}^3P_1 \\ {}^3P_0 \end{cases}$ Splitting $\begin{matrix} {}^3P_2 \\ {}^3P_1 \end{matrix} \Big\rangle = \zeta_{np}$; $\begin{matrix} {}^3P_1 \\ {}^3P_0 \end{matrix} \Big\rangle \frac{1}{2}\zeta_{np}$

Hence we expect to find parallel lines for the three ^3p components in the graph of δ vs. T_m.



When the series are unperturbed we find st. lines converging to a point.

The Slater theory (1929) explains how these relative term values fall on a st. line (cf. Condon & Shortley)

Theory Energy is expressed in terms of three parameters.

F_k's measure the Coulomb interaction between electrons
∴ energy depends on the l's of the orbit.

G_k's measure the electrostatic interaction due to exchange interaction ∴ depends on the s orbital values

ζ_{nl} measure the fine structure due to the separation due to spin orbit interaction.

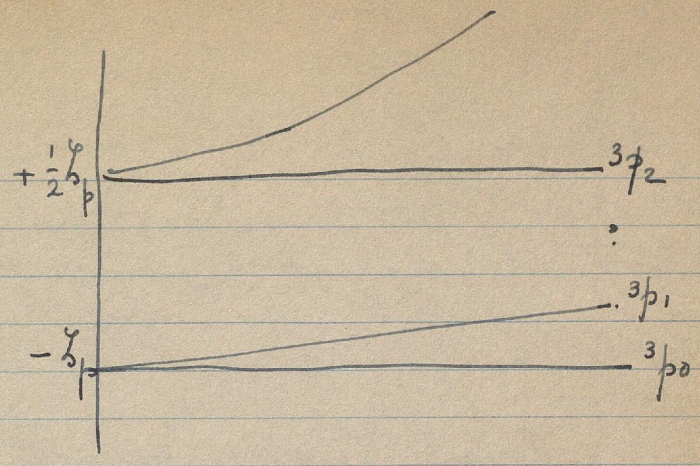
Thus $\quad ^1p = F_0 + G_1$

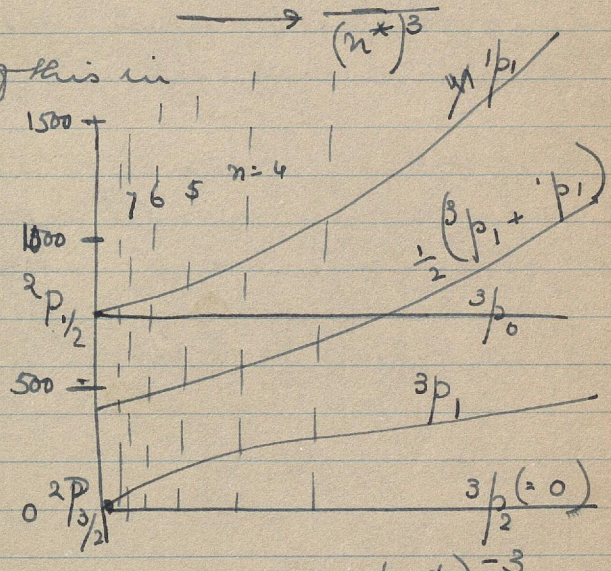
$$^3p = F_0 - G_1 \begin{cases} + \frac{1}{2}\zeta \\ - \frac{1}{2}\zeta \\ - 1\,\zeta \end{cases} \qquad \text{Here } \zeta \ll G.$$

If the p electron has fixed n and the s electron takes different n values,
Terms are $p\,(^2p_{3/2}, {}^2p_{1/2})\,ns$

Thus there are two series limits.
Here at high n values $\zeta \gg G_1$

$$^3p_2 = F_0 - G_1 + \tfrac{1}{2}\zeta_p$$
$$^3p_0 = F_0 - G_1 - \zeta_p$$
$$\left.\begin{matrix} ^3p_1 \\ ^1p_1 \end{matrix}\right\} = F_0 - \tfrac{1}{4}\zeta_p \pm \sqrt{\left(G_1 + \tfrac{1}{4}\zeta_p\right)^2 + \tfrac{1}{2}\zeta_p^2}$$





We have an illustration of this in Ne I $2p^5(^2P)\,ns$.

Thus plotting against $(n^*)^{-3}$ is a more convenient method for studying the separation between the levels.

For terms of the kind $p^2(^3p)\,ns$ gives ^2p, ^4p

$$^2p_{1/2},\ ^4p_{1/2} = \tfrac{1}{2}G_1 - \tfrac{3}{4}\zeta_p \pm \tfrac{1}{2}\sqrt{9G_1^2 + G_1\zeta_p + \tfrac{1}{4}\zeta_p^2}$$

$$^2p_{3/2},\ ^4p_{3/2} = \tfrac{1}{2}G_1 \pm \tfrac{1}{2}\sqrt{9G_1^2 + 4G_1\zeta_p + \zeta_p^2}$$

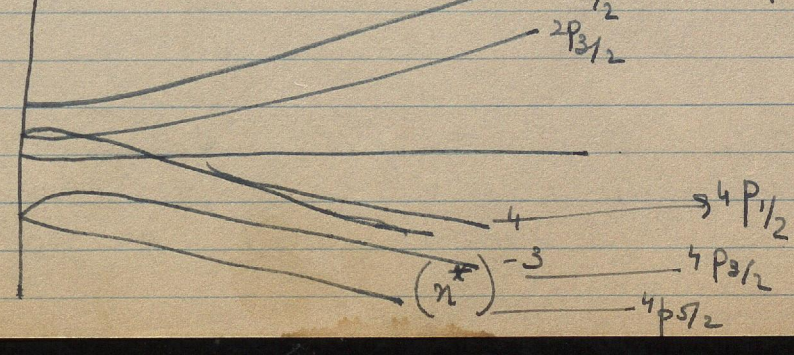
$^2p_{3/2}$ has the $+\frac{1}{2}\sqrt{\cdots}$ & $^4p_{3/2}$ has $-\frac{1}{2}\sqrt{\cdots}$

$$^4p_{5/2} = -G_1 + \tfrac{1}{2}\zeta_p.$$

Curves are drawn for E/ζ_p vs G_1/ζ_p

$p^4(^3p)\,ns$ values are obtained by reversing the sign of ζ_p.

A good illustration is found in Fl I $2p^4(^3p)\,ns$

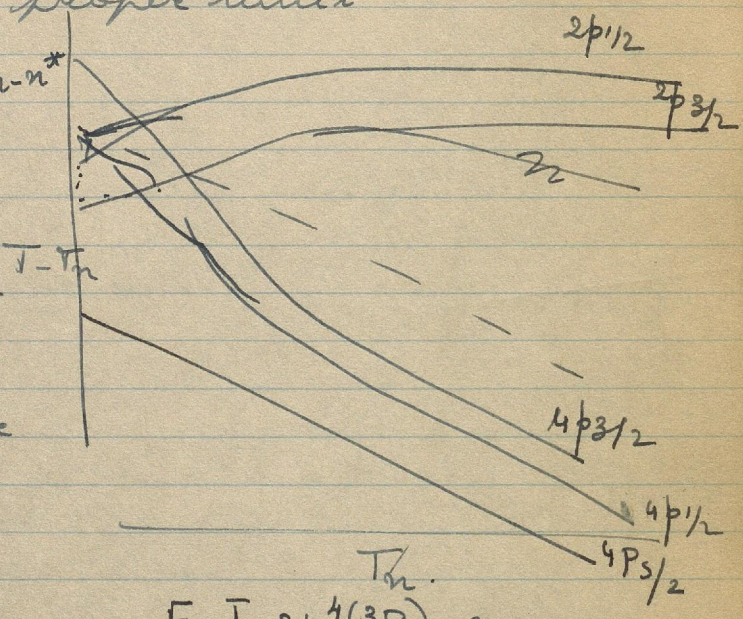


To find the series limit from the higher terms in cases like the above we plot the quantum defect against the n.

The term value for the Ritz formula should be counted from the proper limit

Due to perturbation the Ritz formula curve departs from the predicted st. line

If j value occurs only once the j curve will be st. line. If there is more than one j value, the average will give a st. line for Ritz Δ curve.



F I $2p^4(^3P)ns$

If l value of running electron increases we get to very simple structures.

e.g. $2p^5(^2p)nf$ in Ne I.

The Slater formula will contain ζ_p, F_2, G_2, G_4, ζ_{nf}

There are in all 12 levels.

Some j values occur 2 or three times.

Hence the equations are complicated.

If ζ_p is constant. ζ_{nf} is very small.

$F \gg G$.

F's measure Coulomb repulsion

For $2p^5(^2p)nd$ ~~goes~~ has ζ_p F_2 G_1, G_3 & ζ_{nd}

G_2 & G_4 in f terms are quite small.

Thus structure is determined by ζ_p & F_2.

It is not j-j coupling since ζ_{nd} is very small.

It is not L-S coupling since G is small.

Thus we have pair coupling.

F_2 goes down. $\zeta_p \gg F_2$

We can neglect interaction between ~~terms of~~ levels of the two groups. X

The structure can be given in very simple formulae

	j	E		
$^2P_{1/2}$	4, 3	$+\frac{1}{2}\zeta_p$		~780 cm^{-1}
	3, 2	$+\zeta_p$		
$^2P_{3/2}$	5, 4	$-\frac{1}{2}\zeta_p$	$-5F_2$	< 25 cm^{-1}
	4, 3	..	$+10F_2$	
	3, 2	..	$+3F_2$	
	2, 1	..	$-12F_2$	

E is counted from centre of gravity of the groups

In Ne I the pairs cannot be easily separated.

$p \quad f$

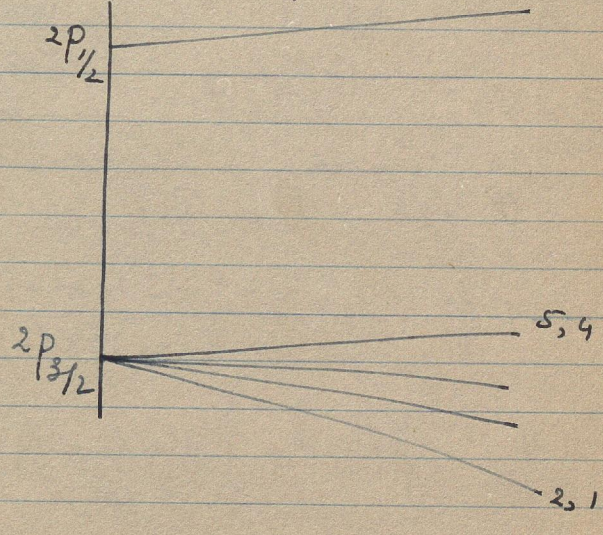
$l_1 s_1 \quad l_2 s_2$ $\qquad \vec{l}_1 + \vec{s}_1 = \vec{j}_1$

l_2 & s_2 have very weak coupling. $\vec{j}_1 + \vec{l}_2 = \vec{K}$, the intermediate quantum numbers (Racah)

$\vec{K} + \vec{s}_2 = \vec{J}$

Racah has given general formula for the various configurations of this type.

For Ne Total splitting within a group < 25 cm



Pair coupling:

This is of wide use in atomic spectra. We may approach it ~~either~~ from the Slater formula & simplify it or we may treat it from the vector model.

$(l_1, s_1)\ l_2\ s_2$

Pair coupling assumes that there is strong interaction between l_1, s_1, & weaker bet (l_1, s_1) & l_2 & the weakest is with s_2.

$$l_1 + s_1 \rightarrow j \quad ; \quad j + l_2 \rightarrow K \quad ; \quad K + s_2 \rightarrow \vec{J}.$$

$J = K \pm \tfrac{1}{2}$.

The conditions for pair coupling to exist is & Strong interaction in the core.

$$\zeta_{core} \gg F_2 \gg \left[\text{all other parameters } F_4, G_1, \text{ Spin orbit interaction of the running electron}\right]$$

With increasing ~~Z~~ n, F_2 & other parameters become smaller. ζ_{core} remains the same ~~Thus~~ & Thus this condition $\zeta \gg$ holds with high n.

The higher the l-value the better this condition is fulfilled.

The case $l_2 = 0$: ~~We cannot~~ Pair coupling is the same as j-j coupling.

$l_2 = 1$ (running p ~~be~~ electron) Situation is intermediate.

$l_2 = 2$ we get fairly good approximation to pair coupling at least for lighter elements.

With increasing ~~atomic no~~ nuclear charge the $\vec{K}, \& \vec{s}_2$ will increase more rapidly & we come to j, j coupling.

Racah Phys Rev. 61 537 (1942)

$$f_2 = -\frac{6h^2 + 3h - 2j(j+1)l(l+1)}{4j(j+1)(2l-1)(2l+3)}$$

j is the j value of the core : $\vec{l}_1 + \vec{s}_1 = \vec{j}$

l is l-value of the running electron.

$$h = K(K+1) - j(j+1) - l(l+1) \qquad \vec{K} = \vec{j} + \vec{l}_2$$

Notation for this kind of coupling.

$p^5(^2P_{3/2})\, nf(4\tfrac{1}{2})_{5,4} \rightarrow nf(4\tfrac{1}{2})_{5,4} \rightarrow nf_{45}$

$(^2P_{1/2})\, nf(3\tfrac{1}{2})_{4,3} \qquad nf'(3\tfrac{1}{2})_{4,3} \qquad nf'_{34}$

Pair coupling applies not only to this case of two limits $^2P_{3/2}$ and $^2P_{1/2}$

Another case — First spectra of halogens

$^3P_2\ nd$ K values (4), (3), (2), (1), (0) — $(0)_{1/2}$

$^3P_1\ nd$ (3), (2), (1)

$^3P_0\ nd$ (2)

e.g. d series of Fl I.

Case where pair coupling is best realized is from f on in Ne I

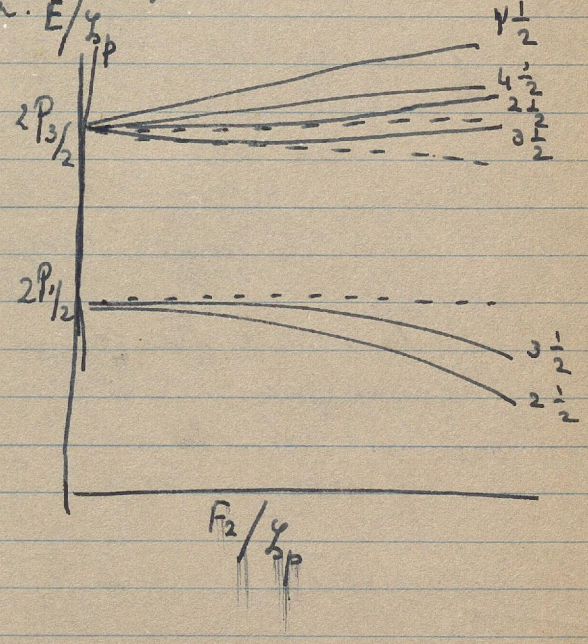
The scheme assumes that the distance between the two limits $^2P_{3/2} - {}^2P_{1/2}$ is too large compared to the separation within the group.

Thus if we have $p(^2P)nf$

the splitting of the limits is much smaller than for 5p core.

The 4th example is N II.

The same comparison was made for $p(^2P)5g$.

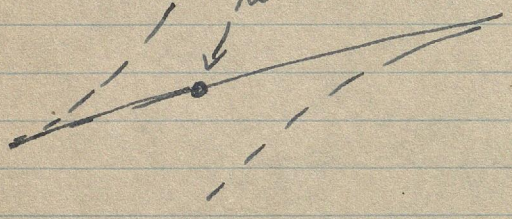


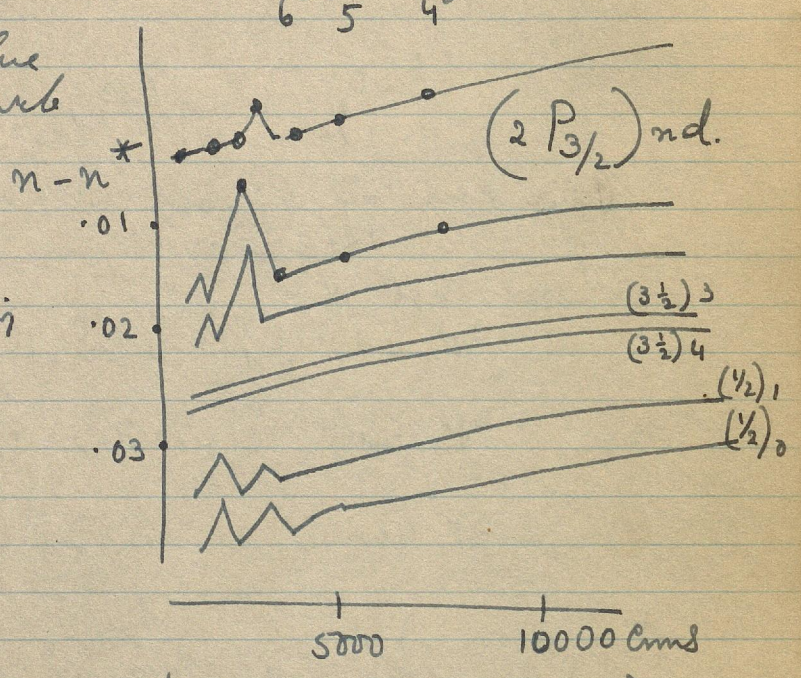
Perturbed Series especially with regard to series perturbations in rare gases.

Shenstone & Russell 1932 discussed the effect in general.

Two levels with same j value & same parity may perturb each other.

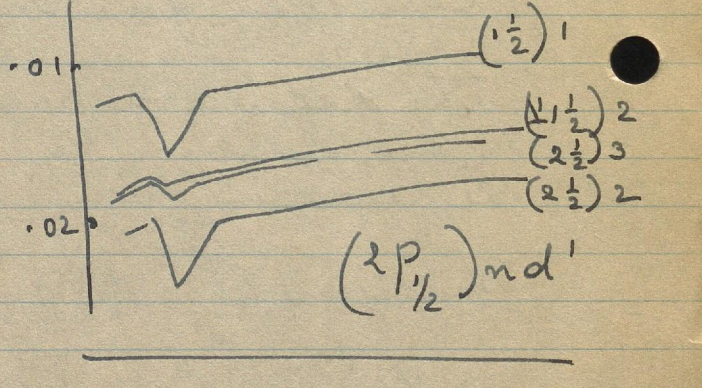
In Neon the primed and unprimed levels perturb each other.





The modified form is

$$n - n^* = a + bt + \frac{\alpha}{T_n - T_0}.$$



If there is more than one perturbing level we get $\sum \frac{\alpha_i}{T_n - T_{d_i}}$.

In rare gases we have two series perturbing each other. Hence many terms in the Σ summation.

There are relations between α_i's which simplify the expression.

If T, δ & T', δ' denote the two series

Term value $-\Delta T_k' = \Delta T_i$; [Quantum defect] & $\Delta\delta_i = \alpha_R / (T_i - T_R')$ for any i

$$\& \quad \Delta\delta_k' = \frac{\alpha_i}{T_R' - T_i} \quad \text{for any } R.$$

$$\Delta T = \frac{2R}{(n^*)^3}\,\Delta\delta$$

$$\alpha_K \left(n_K^*\right)^3 = \alpha_i \left(n_i^*\right)^3 = \alpha \quad \text{a constant.}$$

$$\delta_n = a + b t_n + \ldots\ldots \alpha \sum_K \left(t'_K\right)^{3/2} \cdot \left(T_n - T_K'\right)^{-1}$$

~~Same~~ where $t = \frac{1}{\left(n^*\right)^2}$

$$\delta_n' = a' + b' t_n' + \alpha \sum_i \left(t_i\right)^{3/2} \left(T_n' - T_i\right)^{-1}$$

Interactions are most pronounced between the same K values.

Radon limit separation is 30,000 ; the upper system has completely disappeared & hence perturbations too have disappeared.

Absolute wavelength Standard.

The sharper the profile, the more preferable the line would be.

The main source of line width in all lines which need be considered is the Doppler width.

Doppler width is $\propto \sqrt{T/M}$.

T is the lowest temp. at which vapour pressure of the element permits excitation

Hg $M = 200$ T lowest is $10\,^{\circ}C = 280^{\circ}K$ $\sqrt{T/M} = \sqrt{\frac{280}{200}} = 1.2$

Kr T is $63^{\circ}K$ $\sqrt{T/M} = \sqrt{\frac{68}{86}} = 0.9$

Hence Kr is ~~narrow~~ (3/4) narrower than Hg.

Cd in Michelson's $\sqrt{500/114} = 2.$

Xe $\sqrt{T/M} = \sqrt{77/136} = .75$ .55

The secondary standards are those which are most used. The standard in Paris is very rarely referred.

One can reduce the Doppler width by collimation.

At present the only field where this high accuracy of length measurement ~~has to be~~ is needed is spectroscopy.

How much narrower is the natural line width?

Best lines are those from metastable states – the forbidden lines.

The green auroral line has high Doppler width

Spectologists want a line which can be filtered out from all other lines of the source.

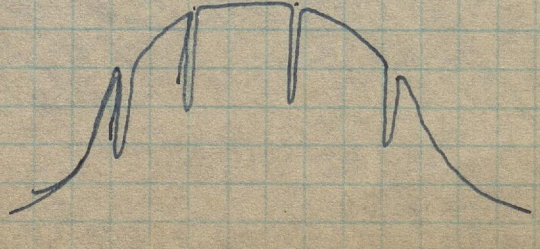
Jackson observed the resonance line in Ga I

λ 4033·4172

This ~~has been~~ is 3 or 4 times sharper than the Hg + Kr line.

The half width is ·005 cm^{-1}.

The resonance emission line is sent through an atomic beam. The fine structure of the line is seen.



The krypton line which would be used directly as standards are

Engelhardt: Proc Verb. Com. Int. Pet M. 2nd Series (poids et mesures) Vol 23 (1953) p 165.

A lamp with internal electrodes is kept at triple point of Nitrogen. Vapour pressure is .03 mm Hg. at 63°K.

λ 6056 has been recommended in particular.

Engelhart worked with Xe at 80°K. There has been no good line in the yellow region.

The movement at present is away from the mercury.

In 1960 the general assembly of weights and measures will meet.

Xe I Line Intensities

The following table gives photoelectric measurements on the intensity of Xe I lines. The values have been corrected for spectral sensitivity variations. The ~~the~~ source was a sealed off tube of 8 mm pyrex, about 4" long with a uranium side arm. The excitation was by means of the Raytheon oscillator at 2450 ~~50~~ ~~me~~/sec. The original filling of the tube was 16 mm and it is believed not to have changed appreciably due to any ~~the~~ cleanup during discharge. The tube has been newly sealed off and it was for the first time being put to use.

The general reproducibility of the results was good as long as slit width was maintained constant. But most lines being diffuse a different slit width is likely to give discordant results.

The slit widths employed were .15 mm exit slit and .35 mm entrance slit for the regions

(a) 3630 – 4843 A.U. filter 4305

(b) ~~3~~4843 – 7119 A.U. filter 3384

and ~~7~~ .3 mm exit slit and .7 mm entrance slit for the region

(c) 7119 – 9800 A.U. filter 2434

The values were chosen as they were adequate for integrating the intensity of ~~two~~ all except the very ~~broad lines~~ diffuse lines.

~~The scale is identical with that of~~

The scale has been so chosen that the estimated intensities of the weakest photographic determinations now in progress will all be positive.

3.3.54.

~~2075~~ 2015 #1

Broadening Asymmetry and Shift of Rubidium Resonance lines under different pressures of helium and argon up to 100 atmospheres.

Ch'en - P.R. 58 p 1057, 1940.

In addition to He & A upto 100 atmos., Hydrogen was used up to 20 atm. Up to a relative density of 46, the broadening is proportional to the concentration of the He or A gas. The slopes of the half-width Vs relative density curves are 0.735 cm^{-1} and .594 cm^{-1} per unit relative density of He for the $^2P_{3/2}$ and $^2P_{1/2}$ components respectively. He produces a violet, A a red asymmetry. The degree of asymmetry increases as the concentration of the foreign gas increases & is comparatively much greater for argon. For argon the asymmetry of the $^2P_{3/2}$ component is much greater than that of the $^2P_{1/2}$ component, while for He the reverse is true. A

Argon produces a greater shift than helium. The former produces a strong red shift & the latter a violet-shift. For both gases the shift of the $^2P_{1/2}$ component (7947.) is greater than that of the $^2P_{3/2}$ (7800) component. For He the shift appears to be proportional to the relative density and the shift of the longer wavelength component is twice as that of the shorter wavelength component; while for argon the shifts of the doublet components are quite close, & the relation between shifts and relative densities obeys in general the 3/2 power relationships.

Optical collision diameters as calculated from the half-width data are 13.37 A & 7.753 A for Rb-A and Rb-He respectively.

From the measurements of the total absorption from the line contours, f-values and the transition probabilities were evaluated.

Pressure effect on the second doublet.

Ch'en PR 58, 1058, 1940.

Pressure effect of N_2 & H_2 on the second doublet was studied upto ~~12~~ 13 atmospheres.

For N_2 & H_2 the $^2P_{3/2}$ component broadens more

conspicuously than the $2P_{1/2}$ one; and the relationship between half-width and relative density is linear. N_2 produces a red shift for both components while H_2 has a weaker red shift for $2P_{3/2}$ & a stronger violet shift for $2P_{1/2}$. The departure from a linear relationship between shift and the density of the perturbing gases is quite manifest.

Self-broadening and foreign gas broadening in the infra-red absorption spectrum of HCN.

Foley – 61, 545 A, 1942.

The shapes of 20 lines in the 14μ absorption band of HCN have been examined with high resolution at a series of pressures up to 58 Cm of Hg with 2 Cm pressure of HCN the lines have also been measured with pressures of HCl present as a foreign gas perturber. In both cases the perturbing interaction is between polar molecules of known dipole moments and thus form an especially favorable case for comparison of the observed absorption coeff with the values given by the theory of pressure broadening. The observed intensity of transmission through the gas $I(\nu)$ is related to the absorption coeff $\alpha(\nu)$ by

$$I(\nu) = \int_{-\infty}^{\infty} d\nu' \cdot p(\nu - \nu') \cdot e^{-\alpha(\nu')\ell}$$

where ℓ is the path length in appropriate units, and $p(\nu - \nu')$ is a function giving the spreading effect of slit width. By numerical solution of this integral equation the absorption coeff was obtained as a function of the frequency. The shapes of the lines and the shifts are compared with the theoretical results derived by Dennison & Foley.

More complete account of the self-broadening of the 14μ band of HCN at pressures of 2.5 Cm, 16 Cm, 40 Cm and 58 Cm is given in

Foley PR 69 p 628 1946.

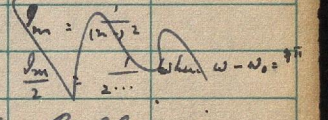
Form 104-H Addison-Wesley Press, Inc., Cambridge 42, Mass. Printed in U.S.A.

Pressure broadening of Spectral lines

Foley: PR 69 616 1946.

Abstract- The Fourier Integral expression for the intensity distribution in a pressure broadened line is derived from the quantum radiation theory with an adiabatic collision approximation. The phase shift approximation to the solution is obtained with the actual distribution of phase shifts taken into account. It is shown that in general there is a shift in line position as well as a line broadening both proportional to the pressure. The ratio of the shift to the broadening depends only on the power of the inter molecular distance with which the interaction decreases. Experimental values of this ratio in foreign gas broadening are on the average consistent with the inverse sixth power. The predicted line widths are slightly higher than those given by Weisskopf. Good agreement with the observed line width is found for most of the alkali metal absorption lines. Calculated line widths and shifts are given for the vibration-rotation lines of linear polar molecules. A method for treating non-adiabatic collisions is given. The conditions for which the Lorentz line form transforms to the Mensenan type line form are indicated. It is shown that the Jablonski wave mechanical treatment of translational motion leads to the same line forms as the Fourier integral method under the proper physical conditions.

(1906)
The Lorentz theory Assume 1) the radiating atom is ~~to be~~ a classical radiating oscillator, 2) the atom has a definite collision radius a 3) each collision either stops the radiation or changes the phase by an arbitrary amount 4) the Fourier integral analysis of the wave train yields the observed frequency distribution of the spectral intensity.



The dispersion line form is given by

$$I(\omega) = \frac{c}{\pi} \frac{n\pi a^2 \bar{v}}{(n\pi a^2 \bar{v})^2 + (\omega - \omega_0)^2}$$

The ~~half~~ half-width in angular frequency units is

$$2n\pi a^2 \bar{v}$$

where n is the number of atoms per c.c.,
a is the collision radius, $\bar{v}$ the mean velocity of the radius.

Hence 1) half-width is proportional to pressure (a result which is experimentally true up to several atmospheres of pressure)

2) Assuming a suitable value of a, the line shape can be plotted for I vs ω and the line shape is found to agree with expt. in many cases, particularly of self-broadening.

But the theory furnishes no value for a & hence neither for half-width.

The Weisskopf Theory (1932)

Assume 1) The radiating atoms is a classical oscillator. 2) Frequency varies in time according to the collision perturbations on the system. The intensity distribution is

$$I(\omega) = \left| A \int_{t_i}^{\infty} e^{-i\left\{\int_{t_i}^{t} \omega'(x)\,dx\right\} + i\omega t} \cdot dt \right|^2$$

where $\omega'(t) = \dfrac{\mathcal{E}_i(t) - \mathcal{E}_f(t)}{\hbar} = \omega_0 + \dfrac{P_i(t) - P_f(t)}{\hbar}$

$P_i(t)$ and $P_f(t)$ are the collision perturbations of the initial and final radiation states of the atoms and $\mathcal{E}_i(t)$ and $\mathcal{E}_f(t)$ are the corresponding total energies of these states.

Time t_i corresponds to the initial time of the radiation process.

Assume 3) Duration ~~of perturbed~~ collision is small compared to the interval between collisions

Thus the main effect of the perturbation is to produce phase shifts in the oscillation.

Assume 4) all phase shifts with magnitudes greater than unity are arbitrary phase shifts and all those less than unity are negligible.

This enables evaluation of the expression for $I(\omega)$

The result gives a Lorentz type line form. The collision radii are given directly from the force law. If the force law is such that the interaction energy varies as the inverse third power of the separation distance, the collision radius is

$$a = \sqrt{\frac{2\beta}{v}} \quad \text{where } \beta = \frac{P_i(t) - P_f(t)}{\hbar} \cdot R^4$$

If interaction energy varies as the inverse 6th power of distance,

$$a = \left\{\frac{3\pi\beta}{8v}\right\}^{1/5}$$

The phase shift approximation is valid for low densities and high velocities of gas molecules.

The 4th assumption leads to the result that the shift of the ~~can~~ line-centre is not contained in the expression.

Kuhn & London Theory (Phil Mag 18, 983, 1934)
modified by Margenau Phys Rev. 48, 755, 1935

The emitting atom is supposed to be stationary. It emits different frequencies dependent on the perturbation of neighbouring atoms. The intensity of any one frequency is proportional to the time for which that frequency is emitted.

The effect has to be summed over all the perturbing atoms which act on the atom.

The line form is

$$I(\omega) = \frac{2\pi}{3}\sqrt{\beta}\cdot\frac{n}{\omega^{3/2}}\left\{e^{-\frac{\pi\lambda}{\omega}}\right\}$$

where $\lambda = \frac{4\pi^2\beta n^2}{9}$, n is the density.

This formulation is valid for low ~~density~~ velocity and high density.

Jablonski Theory P. R. 68, 78, 1945.

A treatment similar to that of the Franck Condon principle for discrete vibrational transitions.

Foley Theory Derivation of the Classical Fourier Integral.

Assume 1) that the quantum theory of radiation applies also to the case of interacting gas atoms and molecules. 2) Motion of the molecules is given by the classical theory. 3) In the Hamiltonian the coordinates of the colliding atoms appear as parameters, not as dynamical variables. 4) Molecular interaction is a time dependent perturbation on the radiating system.

The ranges of the interaction forces which ~~Co~~ are important in line broadening are ~~very much higher than~~ many times greater than 1 or 2 A.U. (the degree of accuracy in the determination of the ~~for~~ position of the molecule.

$$H = H_1(p_l, q_l) + H_2(p_l, q_l, Q_i(t))$$

$$+ H_3(p_l, q_l, p_s, q_s) + H_4(p_s, q_s)$$

~~Coto~~ $$= H_1 + H_4 + L$$

H_1 is the Hamiltonian for the isolated molecule

H_4 is the energy of the charge free radiation field

H_2 is energy due to the interaction of the other molecules on the given molecule, & contains the molecular coordinate $Q_i(t)$

H_3 is the energy of interaction of the radiation field with the molecule.

The solution of $(H_1 + H_4)\psi^\circ = W\psi^\circ$ gives ψ as the product of wavefunctions of atomic systems and of radiation field oscillators.

The complete wavefunction Ψ viz that for $H_1 + H_4 + L$ is expanded in terms of ψ°'s and inserted in the wave eqn. This gives the set of equations for the growth of the a_k states.

The state eqns which do not involve the optical

Foley Theory (Contd)

transitions are of the form $\dot{a}_n = -\frac{i}{\hbar} V_m^n(t)\, a_m(t) \cdot e^{-\frac{i(E_m - E_n)t}{\hbar}}$ (9)

where V_m^n is the matrix element of H_2.

For adiabatic collision conditions the solution is

$$a_n(t) = \frac{V_m^n(t)\, a_m(t)}{E_m - E_n} \cdot e^{-\frac{i(E_m - E_n)t}{\hbar}} \qquad \text{for } V(0) = 0.$$

The eqns containig ~~no~~ of real transition matrix elements are of the form

$$\dot{a}_f = S_i^f a_i\, e^{-\frac{i(E_i - E_f - \hbar\omega_s)t}{\hbar}} - \frac{i}{\hbar} V_n^f a_n(t)\, e^{-\frac{i(E_n - E_f)t}{\hbar}}$$

in which S_i^f is the ordinary matrix element for spectral transition

For self-broadening, the effect is due to two causes: ~~The~~ the resonance interaction of like molecules and the Van der Waals interactions. Hence the expression for the intensity is the sum of two terms

Phase shift solution of the Fourier Integral:

The phase-shift approximation assumes that the ~~for~~ duration of a collision is vanishingly small. The forces are considered to be cut off at a collision distance ρ_0 and the phase shifts cutoff at a corresponding value α_0 (eventually time is extended to ∞)

The expression for the intensity gives a half width $\frac{2(1-A)}{T_0}$ (where T_0 is the mean time between collisions

A is the average value of $\cos\alpha$, α is the phase shift)

and there is a shift of line centre $= \frac{B}{T_0}$

where B is the average value of $\sin\alpha$.

$$\alpha = \int_{-\infty}^{\infty} \frac{V_i - V_f}{\hbar}\, dt \quad , \text{ where } V \text{ is the interaction energy and is assumed to be of the form}$$

$$V = \frac{B\hbar}{R^p}$$

For resonance broadening phase shifts with positive and negative signs occur with equal probability, and the phase shift distribution $\phi(\alpha)$ is an even function of α.

In foreign gas broadening the phase shifts have predominantly one sign which may be either positive or negative and hence the shift is not zero.

Foreign gas broadening in atomic spectra.

In order to calculate the line broadening and line shift, we have to determine first the electronic dispersion interaction in both levels involved in the optical transition.

For the ground state Margenau's method of polarizability gives faithly accurate value of the dispersion.

Ref Margenau Rev. Mod Phys 8, 1, (1939)

But for the excited state only rough estimates can be given. The reason is that we do not know accurately the atomic interaction forces (the Van der Waals forces) Assuming the inverse 6th power law, ~~the~~ Foley has calculated the ~~Lor~~ broadening in a number of cases. The line width and line shift varies linearly with pressure

The ratio of the shift to half width is ~~de~~ independent of the strength of the interaction and depends only on the power of the ~~interaction~~ separation distance which occurs in the interaction law (i.e. on the n of eqn $F \propto C/R^n$.

But the ratio as calculated by different authors ~~Da~~ varies between .17 and .77 and hence it is not possible to say that the law C/R^6 is verified. However the average is .375 which is very close to the value for the inverse 6th power law.

Self. broadening in Atomic Spectra.

The following mechanism is assumed: ~~If~~ Incident radiation excites the atom (A) to a higher level. The excited atom A transfers its energy to an atom B. Such transfer occurs at each collision. The transfer is equivalent to a damping of the oscillation of the radiating atom. The damping causes a dispersion of the line. The half-width of the line is equal to the decay constant of the oscillation.

The half width of the resonance broadened line is

$$\Delta\nu_{1/2} = 4\pi^3 n \beta_{AV}.$$

where β_{AV} is the average absolute value of the Coeffts in the resonance interaction β/R^3.

Stark Effect

In H_2 atom the eqn is

$$\{(\mathcal{H}^\circ + \mathcal{L}) - (E_0^\circ + \varepsilon_i)\}\{\sum C_{in}\psi_n^\circ + \sum a_{i\sigma}\psi_\sigma^\circ\} = 0.$$

$$\{\mathcal{H}^\circ - E_0^\circ + \varepsilon_{in}^\circ\}\psi_n^\circ = 0.$$

Hence in first order approximation for the degenerate states we have the secular eqn

$$\begin{vmatrix} L_{11}-\varepsilon_i & L_{12} & L_{13}\cdots \\ L_{21} & L_{22}-\varepsilon_i & L_{23}\cdots \\ L_{31}\cdots & & \end{vmatrix} \begin{vmatrix} C_{i1} \\ C_{i2} \\ C_{i3} \end{vmatrix} = 0$$

whence we calculate the n values of ε_i

For the case of $n=2$, all matrix elements except L_{13} & L_{31} are zero so that

$$\begin{vmatrix} -\varepsilon & 0 & L_{13} & 0 \\ 0 & -\varepsilon & 0 & 0 \\ L_{31} & 0 & -\varepsilon & 0 \\ 0 & 0 & 0 & -\varepsilon \end{vmatrix} = 0 \quad \text{so that} \quad \varepsilon = \begin{matrix} 0 \\ 0 \\ -L_{13} \\ +L_{13} \end{matrix}$$

$$L_{13} = \int \psi_1 \mathcal{L} \psi_3 \, d\tau$$

where $\mathcal{L} = Er\cos\theta$

$$\psi_1 = \psi_{2,0,0} = R \cdot \Theta \Phi =$$

$$L_{13} = eE \int_0^\infty r^3 R_2 R_2 \, dr \int_0^\pi \cos\theta \sin\theta \cdot (\cos\theta) d\theta \int_0^{2\pi} e^{i\varphi} d\varphi$$

$$= \frac{3h^3 E}{4\pi^2 m e}$$

Perturbation Theory cf Bohm p 408.

The wave eqn is $\mathcal{H}\psi = i\hbar \frac{\partial \psi}{\partial t}$.

$\mathcal{H} = \mathcal{H}^\circ + \lambda V(x,p,t)$ where $\mathcal{H}^\circ$ is the Hamiltonian for which the solution is known exactly, λV is the perturbing term.

Thus when the hydrogen atom is placed in an electric field $\mathcal{E}$,

$$\mathcal{H} = \left\{-\frac{\hbar^2}{2m}\nabla^2 - \frac{e}{r}\right\} + e\mathcal{E}x. \quad \text{Here } \lambda V = e\mathcal{E}x.$$

In the more general case λV may involve not only x, but also $\vec{p}$ and t.

When $\lambda = 0$

$$\psi_{\lambda=0} = \sum_n C_n u_n e^{-\frac{iE_n^\circ t}{\hbar}}$$

Since $\lambda \neq 0$ C_n is not a constant but varies with time. This method is therefore called method of variation of constants.

$$\psi = \sum_n C_n(t)\, u_n^\circ e^{-i\frac{E_n^\circ t}{\hbar}}$$

$$-\frac{\hbar}{i}\dot{C}_m(t) = \lambda \sum_n C_n(t)\, e^{-i\frac{E_n^\circ - E_m^\circ}{\hbar}t} \cdot V_{mn}$$

where $V_{mn} = \int u_m^{\circ *} \{V(\vec{x}, \vec{p}, t)\} u_n^\circ \, d\tau$

V_{mn} is the m,n^{th} matrix element of V in the representation in which H° is diagonal.

Assume that at time $t=0$, the atom was in the sth state so that

$$C_s(t=0) = 1 \quad \text{and} \quad C_n(t=0)_{n \neq s} = 0.$$

The time-rate of change of C_m is $\propto$ to λ and hence if λ is small we may assume C_n's to remain constant. Thus

$$-\frac{\hbar}{i}\dot{C}_m(t) = \lambda\, e^{-i\frac{E_s^\circ - E_m^\circ}{\hbar}t} \cdot V_{ms}(t)$$

$$\therefore C_m(t) = -\frac{i}{\hbar}\lambda \int_{t_0}^{t} e^{-i\frac{E_s^\circ - E_m^\circ}{\hbar}t} V_{ms}(t)\, dt.$$

This approximation is valid until the C_m terms as calculated from it become very large.

Perturbation Theory for Stationary State wave functions.

$$(\mathcal{H}^\circ + \mathcal{L})\left(\psi_n^\circ + \sum_s a_s \psi_s^\circ\right) = (E_n^\circ + \varepsilon)\left(\psi_n^\circ + \sum_s a_s \psi_s^\circ\right) \quad (1)$$

$$\varepsilon(1 + a_n) = L_{nn} + \sum_s a_s L_{ns} \quad (2)$$

$$a_\sigma (E_n^\circ - E_\sigma^\circ + \varepsilon) = L_{\sigma n} + \sum a_s L_{\sigma s} \quad (3)$$

In first order approximation $\varepsilon^{(1)} = L_{nn}$, $a_\sigma^{(1)} = \dfrac{L_{\sigma n}}{E_n^\circ - E_\sigma^\circ}$ (3a) $a_n = 0.$)

$$\psi_n^{(1)} = \psi_n^\circ + \sum_{\sigma \neq n} \frac{L_{\sigma n}}{E_n^\circ - E_\sigma^\circ} \psi_\sigma^\circ$$

$$\varepsilon(1 + a_n) = L_{nn} + \sum_s a_s L_{ns} \text{ i.e. } \varepsilon^{(2)} = L_{nn} + \sum_\sigma \frac{|L_{\sigma n}|^2}{E_n - E_\sigma^\circ} \quad (3b)$$

Let the ~~canal~~ symbols be altered as follows:

Let $\psi_n = \psi_n^\circ + \sum_s a_s \psi_s^\circ \longrightarrow \psi_s = \sum_n C_{ns} U_n(\vec{x})$ (4)

Bohm p 454

$\mathcal{L} \xrightarrow{\text{i.e. } n \rightleftarrows s \text{ exchanged}} \lambda V$ where λ is small.

$$\left.\begin{aligned} C_{ms} &= \delta_{ms} + \lambda C_{ms}^{(1)} + \lambda^2 C_{ms}^{(2)} + \dots \\ \text{and } E_s &= E_s^\circ + \varepsilon_s = E_s^\circ + \lambda E_s^{(1)} + \lambda^2 E_s^{(2)} + \dots \end{aligned}\right\} \quad (4)$$

~~In the first order~~ These expressions for C_{ms} and E_s maybe inserted into eqn (3) which now has the form

$$C_{ms}(E_s - E_m^\circ) = \lambda \sum_n V_{mn} C_{ns}.$$

Collecting coeffs. of equal powers of λ

$$0 = \delta_{ms}(E_s^\circ - E_m^\circ) + \lambda\left\{\delta_{ms} E_s^{(1)} + C_{ms}^{(1)}(E_s^\circ - E_m^\circ) - V_{ms}\right\}$$
$$+ \lambda^2\left\{\delta_{ms} E_s^{(2)} + C_{ms}^{(1)} E_s^{(1)} + C_{ms}^{(2)}(E_s^\circ - E_m^\circ) - \sum_n V_{mn} C_{ns}^{(1)}\right\} \quad (5)$$
$$+ \lambda^3 \dots.$$

In first order approximation, $\lambda^2 \dots.$ can be neglected

$$C_{ms} = \frac{V_{ms}}{E_s^\circ - E_m^\circ} \quad m \neq s \text{ and } E_s^{(1)} = V_{ss} \quad (5\text{-a})$$

(5-a) is the same as (3-a)

If λ^3 and higher powers can be neglected, we have second order approximation

$$C_{mS}^{(2)} = \frac{1}{E_m^\circ - E_S^\circ}\left\{\sum_{n\neq S}\frac{V_{mn}V_{nS}}{E_n^\circ - E_S^\circ} - \frac{V_{mS}V_{SS}}{E_m^\circ - E_S^\circ}\right\}$$

and $E_S^{(2)} = \sum_{n\neq S}\frac{|V_{nS}|^2}{E_S^\circ - E_n^\circ}$

which is the same as eqn (3-b).

The normalization condition gives the value of $C_{SS}^{(2)}$

$$C_{SS}^{(2)} = -\frac{1}{2}\sum_{n\neq S}\frac{|V_{nS}|^2}{(E_S^\circ - E_n^\circ)^2}$$

The first order value of the energy viz $(E_S^\circ + \lambda V_{SS})$ is the average value of the Hamiltonian $H^\circ + \lambda V$ taken with the zeroth order wave-function

Proof: $$\int \psi_n^{\circ *}(H^\circ + \lambda V)\psi_n^\circ d\tau = \int \psi_n^{\circ *} H \psi_n^\circ d\tau + \lambda\int \psi_n^{\circ *} V \psi_n^\circ d\tau$$

$$= E_n^\circ \int \psi_n^{\circ *}\psi_n^\circ d\tau + \lambda\int \psi_n^{\circ *} V\psi_n^\circ d\tau$$

$$= E_n^\circ + \lambda V_{nn}.$$

Similarly it can be shown that the second order value of the energy is the average value of the Hamiltonian $H^\circ + \lambda V$ taken with the normalized first order wavefunctions.

Proof: Cf Bohm p 456.

This theory applies when the perturbation is turned on Bohm p 458 very slowly. The theory applies also whenever any system has been standing around so long as to become a ~~stationary~~ steady state. In other words the energy levels of a system that has reached a stationary state must be the same as those obtained by turning on a perturbation very slowly. The result is analogous to a similar one in thermodynamics (as for example when we calculate the relations between temperature and efficiency in the ideal ~~Carn~~ Carnot's engine) that the state of thermodynamic equilibrium reached after a long time is the same as that obtained by a quasi-static process.

Fairly Approximation to Energy in Atoms other than Hydrogen.

In hydrogen all levels having same n but different l & m have all the same energy.

The outermost electron of the Xe atom is one dislodged from the $5s^2 5p^6$ shell. The core is

$\{1s^2\ 2s^2 2p^6\ 3s^2 3p^6 3d^{10}\ 4s^2 4p^6 4d^{10}\ 5s^2 5p^5\}$

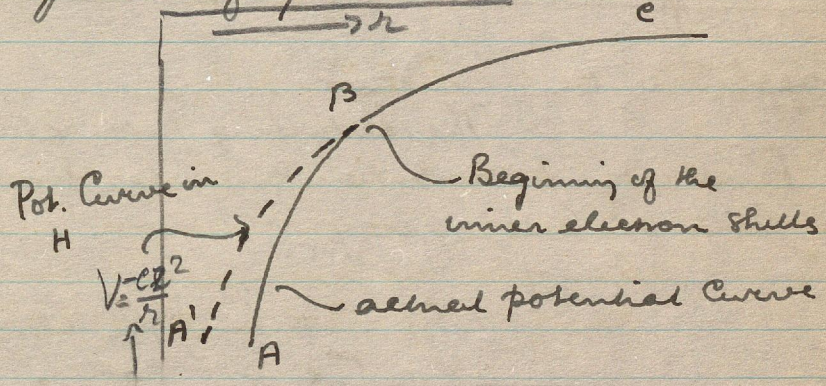
If the Spectral emission electron is entirely outside the core, the core has on the electron the same effect as a hydrogen nucleus & hence the energy levels should be the same as those of hydrogen. But this extreme case is never fulfilled.

The more the electron penetrates the core, the less is the screening effect of the 53 electrons; & correspondingly the greater is the equivalent nuclear charge.

In the case of a single proton & electron the potential energy is $-\frac{e^2}{r}$

If the nuclear charge is Ze the potential is $-\frac{Ze^2}{r}$

The consequence of penetration is that the potential curve is of the shape ABC



In the lighter elements the deviation can be shown to be small & but this is

If the deviation from the Coulomb potential is small the energy

$$V = -\frac{e^2}{r} - \delta V$$

where $-\delta V$ is the correction to the Coulomb potential.

Hence the first order correction in the sth energy level is

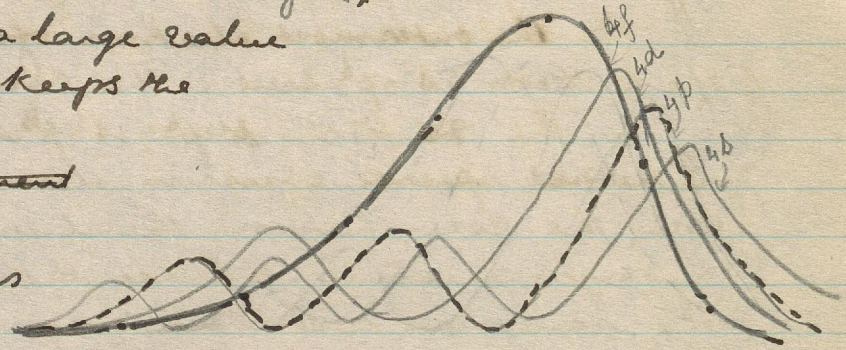
$$\varepsilon = L_{ss} = \lambda V_{ss} = -\int \psi_s^{0*}\, \delta V\, \psi_s^0\, d\tau$$

where ψ_s^0 is the sth eigenfunction of the unperturbed Hamiltonian.

λV_{ss} is large if both δV the change in potential and $|U_s|^2$ the probability amplitude is small at the same region.

δV is large for small value of r.

For a given n, the smaller the value of l the more penetrating is the orbit. For a large value of l the centrifugal potential keeps the electron away from the core.



Thus for a given n, different l's penetration into the core differs according to the l-values And the heavier the atom the greater is the influence of the penetration on the potential energy.

Hence the heavier the atom the greater is the separation of the levels for same n & different l's. In hydrogen levels of same n & different l's are separated all at the same energy level. In Na the difference in wavenumbers for the principal series D_1 D_2 is nearly 17 cm^{-1}. In Xenon there are 6 levels with a maximum difference of 3000 cm^{-1} from $6p_{00}$ to $6p_{01}$.

Stark Effect in Atoms other than hydrogen.

Let a field $\mathcal{E}$ CGSu/cm be applied in the z direction

The perturbing potential is $\lambda V = e\mathcal{E}z$.

First order perturbation vanishes for any eigen state of the unperturbed energy.

Proof

$$\lambda V_{ss} = e\mathcal{E}\int \psi_s^{0*}\, r\cos\theta\, \psi_s^0\, d\tau$$

$$= e\mathcal{E}\int_0^\infty R_s^* r^3 R_s\, dr \int_0^\pi P_s^* \cos\theta \sin\theta P_s\, d\theta \int_0^{2\pi} d\varphi$$

$P_s^* P_s$ is necessarily an even function for any spherical harmonic For the associated Legendre polynomials are an odd or even function of $\cos\theta$ $\cos\theta$ according as $l-m$ is odd or even; and $\therefore$ $P_s^* P_s$ is an even function of $\cos\theta$.

$$\int_0^\pi \cos^{2n+1}\theta \sin\theta\, d\theta = \int \cos^{2n+1}\theta\, d(\cos\theta) = \cos^{2n}\theta\Big|_0^\pi = (-1)^{2n} - 1 = 0.$$

The second order contribution to the energy

$$\lambda^2 E_s^{(2)} = \sum_n \frac{|V_{ns}|^2}{E_s^0 - E_n^0}$$

$$\text{i.e.}\quad \lambda^2 E_s^{(2)} = e^2\mathcal{E}^2 \sum_{\substack{l'=l\pm1 \\ m'=m \\ n}} \frac{|Z|^2_{n'l'm';\,n,l,m}}{\{E^0_{lmn} - E^0_{l'm'n'}\}}$$

If the eigenfunctions are those of the unperturbed Hamiltonian, the V_{ns} vanishes except when $\Delta l = \pm 1$ & $\Delta m = 0$.

Bohm p 460

The shift in energy is $\propto \mathcal{E}^2$ and hence is called the quadratic Stark effect thus to distinguish this effect from the much larger shift in hydrogen where the Stark effect is linear.

The closer are the levels E^0_{sl} the larger will be shift. Thus a large quadratic Stark effect is observed in the lighter alkali metals where the degeneracy has lately been removed.

$E_s^{(2)}$ is proportional to $|Z|^2_{nlm,\,n'l'm'}$.

This integral is roughly proportional to the size of the region in which $|\psi|^2$ are large. Now for a given l, roughly the size of the region in which $|\psi|^2$ is large increases as the square of the principal quantum number. This dependence on n causes two levels involved in a transition to be displaced unequally and hence results in a shift of the spectral line.

Bohm p 471

Classical Interpretation of the Stark Effect:

In hydrogen the Stark effect is linear. The reason is that levels with same n, different l's, are superposed, in other words, there is degeneracy. The quantum mechanical degeneracy has a classical analogue in the case where the frequencies of radial oscillation and rotation are the same. This occurs when the field is of the Coulomb type. And in this case we have reentrant ellipses are the orbit.

With a general law of force the orbits are not closed. The major axis of a quasi-ellipse precesses at a rate determined by the difference between the frequencies of rotation & radial oscillation.

With the Coulomb force the motion is degenerate with respect to the direction of the major axis — i.e. no energy is required to rotate the major axis so long as the focus is unchanged.

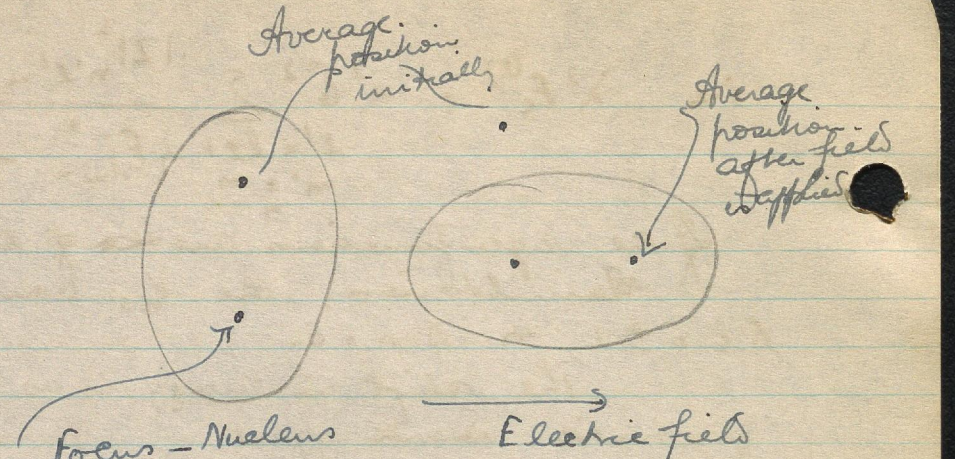
The average position of the electron is not at the focus. An external field, even the weakest, will rotate the ellipse so as to bring the center direction of the average position in the direction of the field.

Thus the average coordinate of the electron is displaced by a quantity d which is of the order of the mean radius of the orbit.

The loss in potential energy is eEd.

This corresponds to the perturbation operator $\mathcal{L} = \lambda V = eEr\cos\theta$ in the linear Stark effect.

A degenerate system like this is infinitely polarizable.



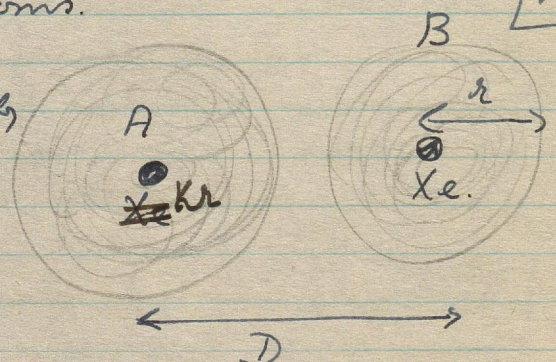
In the non degenerate system, radial and rotational frequencies being different, the ~~orbit~~ orbit precesses rapidly around the nucleus and hence the average position of the electron is at the nucleus itself. When a weak electric field is turned on slowly the orbit slips slightly in the direction of the field. Precession on the other hand serves to make the average position go to $\vec{r} = 0$

The net polarization is the result of a balance between the two effects and gives a mean displacement which is proportional to the electric field. $\therefore d = cE$.

Hence the ~~loss~~ Change in potential energy $= -eEd = -cE^2$

Van der Waals Forces between Atoms.

Bohm p472



Consider two atoms which are gradually brought closer and closer to each other. As long as the distance D is $>$ than $2r$, the electronic charges shield the nucleus & hence in zeroth order there is no net force.

However the electrons are in motion and hence there is a time dependent small field round the nucleus. This field due to A polarizes B and creates a dipole moment in B. Let $\vec{M}$ be the dipole moment. $\vec{M} = P.\vec{E}$ where $\vec{E}$ is the ~~f~~ time dependent field due to A & P is the polarizability of B.

The force on B due to A is $\vec{F} = (\vec{M}\cdot\vec{\nabla})\vec{E} = P(\vec{E}\cdot\vec{\nabla})\vec{E}$.

Though the time average of $\vec{E}$ is zero the time average of $\vec{F}$ is not zero since $\vec{F}$ depends on the second power of $\vec{E}$. ~~Thus~~ When $\vec{E}$ changes in sign

the induced dipole moment makes a compensating charge.

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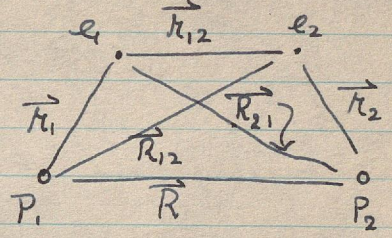
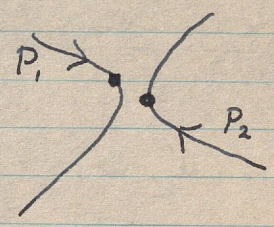
P_1, P_2 are the two nuclei; & e_1, e_2 the two electrons. Assume that the core electrons are bound tightly to the nuclei. ~~Assume~~ (This is valid in the ~~All~~ alkali metals)



Assume that nuclear kinetic energy can be neglected as a first approximation. (~~Re~~ The electron makes 7×10^6 oscillations in the time interval between two collision & hence during any one oscillation of the electron the nucleus is practically at rest ~~of page on xe constants~~. This is essentially the adiabatic approximation. ~~is possible~~



The Hamiltonian is $\mathcal{H} = \mathcal{H}_1(r_1) + \mathcal{H}_2(r_2) + V$.

Total potential energy

$$-e^2\left\{\frac{1}{r_{1A}} + \frac{1}{r_{2B}} - \frac{1}{r_{12}} - \frac{1}{R_{AB}} + \frac{1}{R_{12}} + \frac{1}{R_{21}}\right\}$$

of which the first two terms are included in $\mathcal{H}_1$ & $\mathcal{H}_2$

$$\therefore \quad V = e^2\left\{\frac{1}{R} + \frac{1}{r_{12}} - \frac{1}{R_{12}} - \frac{1}{R_{21}}\right\}.$$

When the atoms are far apart the interaction energy between them can be neglected so that the solution is

$$\psi_{n_1 n_2} = u_{n_1}(\vec{r}_1)\, v_{n_2}(\vec{r}_2)$$

The u's & v's satisfy $\mathcal{H}_1 u_{n_1} = E^0_{n_1} u_{n_1}$ & $\mathcal{H}_2 v_{n_2} = E^0_{n_2} v_{n_2}$.

The perturbation method can be applied if $V \ll \frac{e^2}{r_1}$, or $\frac{e^2}{r_2}$

i.e. if $\frac{r_1}{R} + \frac{r_2}{R} \ll 1$

In that approximation the first term is a dipole of moment

$$\vec{M} = -e\vec{r}_1$$

and the potential due to that dipole at $\vec{R}$ is

$$\varphi = -\frac{e\vec{r}_1 \cdot \vec{R}}{R^3} = -\frac{e}{R^3}\{x_1 X + y_1 Y + z_1 Z\}$$

The field due to the dipole is ~~&~~ $\vec{\mathcal{E}} = -\vec{\nabla}\varphi$

The second atom is a dipole of moment $\vec{M} = -e\vec{r}_2$.
Its energy in the field due to the first dipole is

$$W = +e\vec{r}_2 \cdot -\vec{\nabla}\varphi = e^2 \vec{r}_2 \cdot \vec{\nabla}\left(\frac{\vec{r}_1 \cdot \vec{R}}{R^3}\right)$$

Carrying out the differentiation with respect to $\vec{R}$

$$W = \frac{e^2}{R^3}\left\{\vec{r}_1 \cdot \vec{r}_2 - 3\frac{(\vec{r}_1 \cdot \vec{R})(\vec{r}_2 \cdot \vec{R})}{R^2}\right\}$$

Non degenerate Case.

The matrix elements are ~~of the form~~

$$\iint_{\tau_1 \tau_2} u^{\times}_{n_1'} v^{\times}_{n_2'} \{W\} u_{n_1} v_{n_2} \, d\tau_1 \, d\tau_2$$ where $\{W\}$ is the perturbation operator.

By choosing z axis along $\vec{R}$, $\{W\}$ simplifies to the form

$$\{W\} = \frac{e^2}{R^3}(x_1 x_2 + y_1 y_2 - 2z_1 z_2)$$

The operator is the product of two Stark effect operators.
Since the levels are non-degenerate linear Stark effect is zero. Similarly here $\vec{r}$ average is zero.
The quadratic Stark effect causes a change in energy.

$$\Delta E = \frac{e^4}{R^6} \sum_{\substack{n_1' \neq n_1 \\ n_2' \neq n_2}} \frac{|W|^2}{(E^0_{n_1} + E^0_{n_2}) - (E^0_{n_1'} + E^0_{n_2'})}$$

$|W|$ is the matrix element for the operator $\{W\}$ between (n_1', n_2') state and (n_1, n_2) state.

The change in energy is $\propto R^{-6}$ which is in agreement with what Van der Waals' forces imply. The reason for this is that the electric field $\vec{F}$ caused by a dipole is $\propto R^{-3}$; the dipole moment $\vec{M}_2$ caused in atom (2) is $\propto$ to this field. and hence the energy is $\propto$ to the product of $\vec{F} \cdot \vec{M}_2$ i.e. $\propto R^{-6}$.

The sum in the expression for ΔE is large either because 1) x_1, x_2 etc are large, i.e the atoms are large or (2) $(E^0_{n_1'+2}) - (E^0_{n_1+2})$ is small i.e. the levels are nearly degenerate.
In alkalis the levels are nearly degenerate and

Bohm p476

Resonant transfer of excitation energy between atoms.

An important case of degeneracy occurs when an atom in the ground state comes near a like atom in an excited state.

Because the two atoms are alike another state of the same unperturbed energy is brought about by transfer of the energy from one atom to the other.

To simplify the treatment, assume an atom in state $n=2, l=1, m=0$ approaches another in state $n=1, l=0, m=0$. The wavefunction for the two atoms together is

$$\psi_1^\circ = u_1(\vec{r}_1)\, u_0(\vec{r}_2)$$

$u_1(\vec{r}_1)$ shows that the first atom ($\vec{r}_1$) is in the excited state u_1 & the second ($\vec{r}_2$) is in the ground state.

The combined energy is $E_1^\circ + E_0^\circ$

If the first atom were in the ground state and the second in the excited state the wavefunction would have been

$$\psi_2^\circ = u_0(\vec{r}_1)\, u_1(\vec{r}_2)$$

Since the atoms are identical, energy corresponding to ψ_2 is also $E_1^\circ + E_0^\circ$.

This value $E^\circ = E_1^\circ + E_0^\circ$ would be the energy only if there is no interaction between the two atoms, i.e. if the Schroedinger eqn is

$$H^\circ \psi_n^\circ = E^\circ \psi_n^\circ$$

where H° is the sum of H_1° and H_2° for the two atoms, each electron being exclusively in its own field & ψ_n° is $\psi_1^\circ = u_1(\vec{r}_1)\, u_0(\vec{r}_2)$.

Since $\psi_n^\circ = \psi_2^\circ = u_0(\vec{r}_1)\, u_1(\vec{r}_2)$ would equally satisfy the eqn, ψ_1° & ψ_2° are two degenerate states for energy E°.

Now the Schroedinger eqn in this case is not

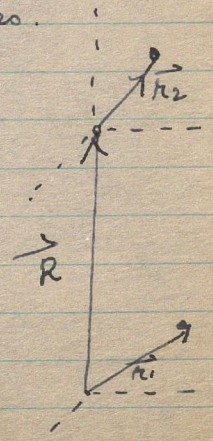
$$H^\circ \psi_n^\circ = E^\circ \psi_n^\circ$$

but $(H^\circ + L)\psi_n = E\,\psi_n$

where L is the mutual energy of the two dipoles.

$$L = \frac{e^2}{R^3}\left\{ \vec{r}_1 \cdot \vec{r}_2 - 3\frac{(\vec{r}_1 \cdot \vec{R})(\vec{r}_2 \cdot \vec{R})}{R^2} \right\}$$

$$= \frac{e^2}{R^3}\left(x_1 x_2 + y_1 y_2 - 2 z_1 z_2\right) \text{ if the } z \text{ axis is along the line of the nuclei.}$$



The perturbed eigenstate ψ_n can be expressed as a linear combination of the degenerate states ψ_1, ψ_2 and of all the other possible combinations.

of the states of the two atoms

$$\psi_n = a_1 \psi_1^\circ + a_2 \psi_2^\circ + \sum C_{n\sigma} \psi_\sigma^\circ$$

where a_1, a_2 are close to unity

and $C_{n\sigma} \approx 0$.

In zero order approximation we have the secular equation

$$\left.\begin{aligned} (L_{11} - \varepsilon)\, a_1 + L_{12} a_2 &= 0 \\ L_{21} a_1 + (L_{22} - \varepsilon) a_2 &= 0 \end{aligned}\right\} \therefore \begin{vmatrix} L_{11} - \varepsilon & L_{12} \\ L_{21} & L_{22} - \varepsilon \end{vmatrix} = 0.$$

Now $L_{11} = \int \psi_1^{\circ x} \mathcal{L} \psi_1^\circ \, d\tau$ etc.

$\mathcal{L}$ has three terms $\propto x_1 x_2$, $y_1 y_2$ & $-2 z_1 z_2$.

But since ψ_1°, ψ_2° have been $\psi^\circ = u_1 u_0$ have both m's $= 0$ $\Delta m = 0$ and hence $x_1 x_2$ & $y_1 y_2$ give matrix elements which reduce to zero (Recall $x + iy$ change to $u = x + iy$ & $v = x - iy$ i.e. to $re^{i\varphi}$, $re^{-i\varphi}$ & $\int_0^{2\pi} e^{im\varphi} d\varphi = 0$ unless $m = 0$.)

Hence only the term $-2 z_1 z_2$ need be considered.

$$L_{11} = -\frac{2e^2}{R^3} \int u_1^*(\vec{r}_1)\, u_0^*(\vec{r}_2) \{z_1 z_2\}\, u_1(\vec{r}_1)\, u_0(\vec{r}_2)\, d\tau$$

In this the integral over θ_1 is

$$\int_0^\pi \cos\theta_1 \cdot \cos\theta_1 \cdot \cos\theta_1 \sin\theta_1 \, d\theta_1$$

from u_1^* for z_1 from $u_1(\vec{r}_1)$ for $d\tau$

and is zero.

Similarly L_{22} is zero.

But $L_{12} = -\frac{2e^2}{R^3} \int u_1^*(\vec{r}_2)\, u_0^*(\vec{r}_1)\, \{z_1 z_2\}\, u_1(\vec{r}_1)\, u_0(\vec{r}_2)\, d\tau.$

where the integral over θ_1 is

$$\int_0^\pi \cos\theta_1 \cdot \cos\theta_1 \sin\theta_1 \, d\theta = \left[\frac{\cos 3\theta_1}{3}\right]_0^\pi = -\frac{2}{3}$$

from z_1 from $u_1(\vec{r}_1)$ for $d\tau$

Thus the secular determinant reduces to

$$\begin{vmatrix} -\varepsilon & (z_1 z_2)_{12} \\ (z_1 z_2)_{21} & -\varepsilon \end{vmatrix} = 0$$

$$\text{i.e.} \quad \varepsilon^2 = \left[(z_1 z_2)_{12}\right]^2$$

i.e. $\varepsilon = \mp (z_1 z_2)_{12}$

$(z_1 z_2)_{12}$ is the off diagonal matrix element

and is equal to

$$-\frac{2e^2}{R^3}\iint u_1^*(\vec{r}_2)\,u_0^*(\vec{r}_1)\{z_1 z_2\}\,u_1(\vec{r}_1)\,u_0(\vec{r}_2)\,d\tau_1\,d\tau_2.$$

$$= -\frac{2e^2}{R^3}\int u_1^*(\vec{r}_2)\{z_2\}\,u_0(\vec{r}_2)\,d\tau_2 \int u_0^*(\vec{r}_1)\{z_1\}\,u_1(\vec{r}_1)\,d\tau_1$$

$$= -\frac{2e^2}{R^3}\,|z_{01}|\cdot|z_{10}| \qquad \text{where } |z_{01}| \text{ is the matrix}$$

element between states 0 & 1 in either of the atoms.

$$= -\frac{2e^2}{R^3}\,|z_{10}|^2.$$

For $\varepsilon = -\frac{2e^2}{R^3}|z_{10}|^2$, $a_1 = a_2$

$$\psi_a = \frac{1}{\sqrt{2}}\{u_1(\vec{r}_1)\,u_0(\vec{r}_2) + u_1(\vec{r}_2)\,u_0(\vec{r}_1)\}$$

and for $\varepsilon = +\frac{2e^2}{R^3}|z_{10}|^2$, $a_1 = -a_2$

$$\psi_b = \frac{1}{\sqrt{2}}\{u_1(\vec{r}_1)\,u_0(\vec{r}_2) - u_1(\vec{r}_2)\,u_0(\vec{r}_1)\}.$$

thus giving the two new eigen functions for the perturbed state.

Both ψ_a & ψ_b contains in equal proportion ~~a~~ excited excitation in 1st atom (or i.e. $u_1(\vec{r}_1)$) and excitation in 2nd atom. That is there is equal probability of the excitation being in either ~~state~~ atom. The same is true if ψ_b is the state vector.

On the other hand if at time $t=0$ the excitation was wholly in atom 1, then we would have a non stationary state. The excitation energy is transferred back and forth ~~with~~ between the atoms with a frequency

$$\nu = \frac{2e^2|z_{10}|^2}{hR^3}.$$

The closer the atoms get together the more ~~freq~~ rapid is the resonant transfer of energy between them.

THE STARK EFFECT.

C&S p. 397

Condon and Shortley.

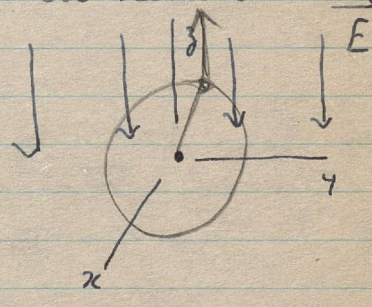
Stark effect was discovered in the Balmer lines of H_2 and in 1913. The theoretical explanation on the basis of the quantized orbits as in Bohr's theory fitted the experimental facts exactly.

The relatively large splitting which exists in Hydrogen is due to the fact that hydrogen levels are degenerate In other atoms the effect is in general very small. ~~Except~~ The effect in other atoms turns out to be large only in the exceptional case when two levels which may optically combine lie close together.

The Bohr theory and the ~~quantum~~ wave mechanics theory give the same values for the first order ~~Stark~~ effect. For the second & higher orders the wave mechanics theory gives a different result and this latter results agrees with ~~exact~~ experimental results. The high order Stark effects are observed when the field is high. And higher fields another aspect of the effect becomes important, namely, ~~the destruction of~~ the field destroys the quantized levels & and the limit of the Balmer series shifts towards the red, in other words, the continuous spectrum encroaches on the part of the frequency scale which is reserved for the line spectrum.

This effect has been observed in Xenon

Let the field be $\mathcal{E}$ in the negative z direction.

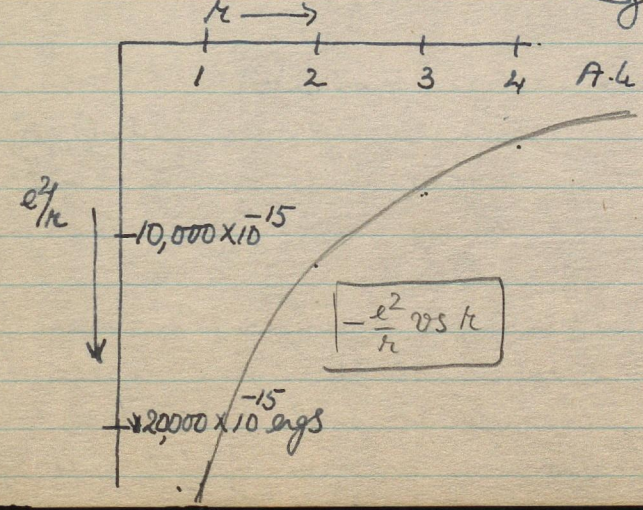


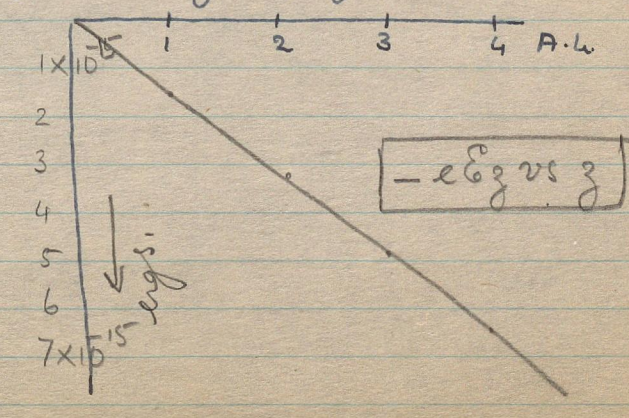
The potential of the electron due to the nucleus is $-e^2/r$, & the potential due to the external field is $-e\mathcal{E}z$.

For $r = 1$ A.U., $e = 4.8 \times 10^{-10}$ e.s.u.

$e^2/r = (4.8)^2 \times 10^{-20} \times 10^8 = 23.04 \times 10^{-12}$ erg.

For $E = \mathcal{E}$ ~~$e\mathcal{E}z$~~ for 100 KV/cm or 10^{-3} V/A.U. of field gives $\mathcal{E}z = 10^{-3} z$ eV $= 1.6 \times 10^{-15} z$ erg.





At $r = z = 1$ A.u., $\frac{e^2}{r}$ is 23040×10^{-15} ergs and $e\mathcal{E}z$ ($\mathcal{E} = 100$ KV/cm) is 1.6×10^{-15} ergs.

At $r = z = 10$ A.u.

$\frac{e^2}{r}$ is 2304×10^{-15} erg & $e\mathcal{E}z = 16 \times 10^{-15}$ erg.

We know that if the Schroedinger eqn

$$\nabla^2\psi + \frac{8\pi^2 m}{h^2}(E - V)\psi = 0 \qquad \text{where } V = -e^2/r$$

is transformed into spherical coordinates we obtain

$$\psi = e^{im\varphi} L_\ell^m P$$

$$\psi = N_{nlm} R \Theta \Phi \quad \text{where } R = e^{-\xi/2} \xi^{l} \mathcal{L}_{n+l}^{2l+1}(\xi); \quad \Theta = (-x^2)^{|m|/2} \frac{d^{|m|} P_\ell(x)}{dx^{|m|}}$$

$$\Phi = e^{im\varphi}; \quad \xi = \frac{2r}{ma}; \quad x = \cos\theta.$$

But with respect to this set of ψ functions the off-diagonal matrix elements of $z = r\cos\theta$ do not all reduce to zero. In fact we know that for $n = 2$, if $\psi_1, \psi_2, \psi_3, \psi_4$ are the four wavefunctions, L_{31} & L_{13} are not zero and the rest are zero. Calculating the matrix elements and solving the Secular equation we can determine the shift in energy.

An alternative procedure is to transform the wave equation into parabolic coordinates. A set of wavefunctions involving four parameters

$$n \quad k_1 \quad k_2 \quad \text{and } m$$

are obtained.

$$n = k_1 + k_2 + |m| + 1.$$

With respect to these wavefunctions the matrix of z is diagonal. The diagonal elements have the value

$$(n k m |z| n' k m) = \frac{3}{2} n (k_1 - k_2) a$$

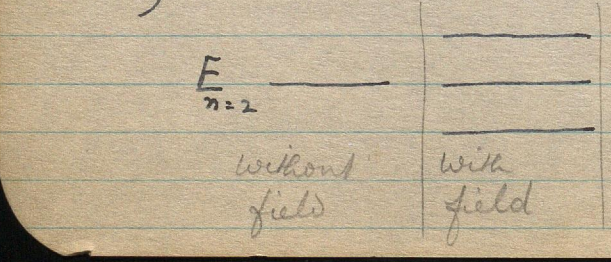
where $a = \frac{h^2}{me^2}$ (m: mass of the electron)

Hence the first order alteration in energy is

$$-\frac{3}{2} n (k_1 - k_2) e\mathcal{E} a.$$

For $n = 2$ the following combinations are possible:

1)	$n = 2$, $m = 0$	$k_1 + k_2 = 1$	$k_1 = 1$	$k_2 = 0$	$\therefore -\frac{3}{2} n (k_1 - k_2) e\mathcal{E} a = -\frac{3e\mathcal{E}h^2}{me}$
2)		or	$k_1 = 0$	$k_2 = 1$	$= +\frac{3e\mathcal{E}h^2}{me}$
3)	$m = 1$	$k_1 + k_2 = 0$	$k_1 = 0$	$k_2 = 0$.	$= 0$.



A single level is thus seen to split into three levels. The shift is the same as from the method of Spherical Coordinates.

$\frac{3E\hbar^2}{me} = \frac{3(\mathcal{E}e)h^2}{4\pi^2 m e^2}$ For $\mathcal{E}$ = 100 kV/cm

$\mathcal{E}e = 10^5$ eV/cm $= 1.6\times10^{-7}$ erg/cm.

$h^2 = (6.62\times10^{-27})^2$ erg^2 sec^2

$= 43.82\times10^{-54}$ erg^2 sec^2.

$m = 9\times10^{-28}$ gm

If e is in esu & r in cm $\frac{e^2}{r}$ is potential in ergs

$\therefore e^2 = (4.8\times10^{-10})^2$ erg cm.

The dimensions of $\frac{E e h^2}{me^2}$ are $\frac{\text{erg}}{\text{cm}}\frac{\text{erg}^2\,\text{sec}^2}{\text{gm erg cm}}$

$= \frac{\text{erg}^2}{\text{cm. gm. cm sec}^{-2}} = \frac{\text{erg}^2}{\text{cm}\times\text{dyne}} = \text{erg}$ the dimensions of energy.

The numerical value is

$$\frac{3\times1.6\times10^{-7}\times43.82\times10^{-54}}{4\pi^2\times9\times10^{-28}\times(4.8\times10^{-10})^2} = \frac{43.82}{4\pi^2\times9\times4.8}\times10^{-13}$$

$\frac{3\mathcal{E}\hbar^2}{me} = 2.57\times10^{-15}$ erg

$= \underline{12.9\ \text{cm}^{-1}}$

In the general case of any values for n, k_1, k_2 & $\mathcal{E}$ we

$V_1(n k_1 k_2) = .0642\, n(k_1 - k_2)\mathcal{E}$ where $\mathcal{E}$ is in kilovolts/cm and V_1 in cm^{-1}

Applying this to our case of $n = 2$, $k_1 - k_2 = 1$, $\mathcal{E}$ = 100 kV/cm.

$V_1 = 12.84$ cm^{-1} which is close to our approximate calculation.

The components of H_α line may be shown to be 15 in all.

H_α is due to $n = 3$ to $n = 2$.

For $n = 2$ levels are at 2, 0 $n - 2$ units away from the unperturbed level. The unit is $.0642\,\mathcal{E}$ cm^{-1}.

For $n = 3$, $m = 1$, $k_1 = \begin{matrix}0\\1\end{matrix}$ $k_2 = \begin{matrix}1\\0\end{matrix}$ $\therefore n(k_1 - k_2) = \begin{matrix}-3\\+3\end{matrix}$

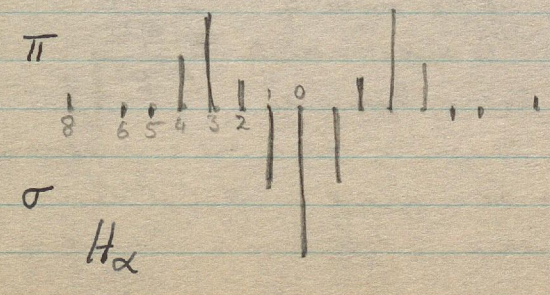
$m = 0$

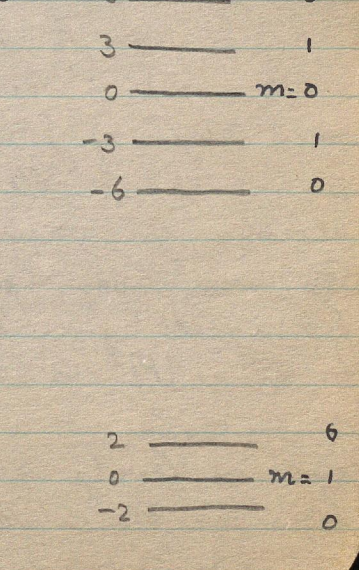
$k_1 = k_2 = 1$ or $k_1 = 0$ $k_2 = 2$ $\left.\begin{matrix}\\\\\end{matrix}\right\}$ $n(k_1 - k_2) = \begin{matrix}-6\\0\\+6\end{matrix}$

$\begin{matrix}2\\0\end{matrix}$

and hence lines should be according to the pattern below

The lines due to $\Delta m = 0$ show ⊥ polarization when viewed transversely. Such is the case with lines in the positions 2, 3 & 4.





The theoretical value of the energy change in the quadratic Stark effect is

$$-\frac{a^3\mathcal{E}^2}{16}\, n^4\{17n^2 - 3(k_1-k_2)^2 - 9m^2 + 19\}$$

Note: always -ve

The theoretical value of the third order Stark effect is

$$\frac{3}{32}\frac{a^5\mathcal{E}^3}{e}\, n^7(k_1-k_2)\{23n^2 - (k_1-k_2)^2 + 11m^2 - 71\}$$

- ve or +ve according as (k_1-k_2) is $\mp$

For a field of 1000 kV for which the unit of shift in linear Stark effect is 6·4 cm^{-1}, the quadratic effect gives a shift of 6·16 cm^{-1} and the third order effect gives ·085 cm^{-1}.

Shift of a particular component can be expressed in the form

$$\Delta\ (cm^{-1}) = \pm a\mathcal{E} - b\mathcal{E}^2 \pm c\mathcal{E}^3.$$

and by reversion of the formula the field strength can be calculated from the shift by the eqn

$$\mathcal{E} = \frac{\Delta}{a}\left\{1 + \frac{b}{a}\frac{\Delta}{a} + 2\left(\frac{b^2}{a^2} - \frac{c}{a}\right)\frac{\Delta^2}{a^2}\right\}$$

General Theory for non-hydrogenic atoms

Condon & Sh. p. 409

The Hamiltonian is of the form $H = H^0 + P_z.\mathcal{E}$

If we know the energy levels and the corresponding eigenfunctions we can calculate the matrix elements of P_z and proceed to apply the perturbation theory. The details of the results so obtained will depend to a large extent on the mode of coupling of the angular momentum vectors and on the amount of configuration interaction.

However certain general features can be pointed out before treating the special cases

1) P_z has matrix components only between states of opposite parity.

2) A state of given J values has matrix components with other states of J values which are $J, J \pm 1$. i.e. $\Delta J = 0$ or ± 1.

3) The order of magnitude of the matrix elements involving electrons in states of total quantum number n will be the same as computed with hydrogenic functions. This is of the order of $6{\cdot}4\, n^2\ cm^{-1}$ for a field of 100 kV/cm. The energy shift is of the order of $\frac{|P|^2}{E-E'}$. Since $|P|^2$ is $\sim 41 \times n^4$, two levels of energy difference greater than $400\, n^4$ produce shift of less than ·1 cm^{-1}. Thus the interaction between levels several thousands of wavenumbers apart is negligible. However the combined effect of an entire series of terms in a given term may be considerable.

4) From the general features of the perturbation theory we know that if the energy of interaction between two states is small compared to the initial separation between the two corresponding levels, the effect of the perturbation will be given quite accurately by the second order formula.

5) For a group of states lying close to each other a more accurate calculation is needed. This requires the solution of the secular equation.

6) The electric displacement of excited states is generally much higher than that of low-lying energy levels and hence the observed pattern is a direct picture of the perturbation of the initial state.

Let $\alpha J M$ be the quantum numbers (principal quantum number(α), quantum number of the total angular momentum(J) and z component along the $\vec{\mathcal{E}}$ of J, (M) of a level on which the perturbation in second order due to all other levels is to be evaluated. Let $\beta_1, \beta_2 \ldots \beta_i \ldots$ be the principal quantum number of any other level. In any given β level, only those sublevels for which $J' = J$ or $J \pm 1$ and $M' = M$ or $M \pm 1$ give non vanishing matrix elements for the operator $\{\vec{\mathcal{E}} e r \cos\theta\}$ The second order displacement in the energy level is

$$\Delta(\alpha J M) = \frac{\delta^2}{hc}\left\{J^2 a_- + (J+1)^2 a_+ - (a_+ + a_- - a_0) M^2\right\}$$

where $a_- = \sum_\beta \frac{|\alpha J \{P\} \beta, J-1|^2}{E_{\alpha J} - E_{\beta J-1}}$ — +ive or −ive according as $E_{\alpha J} - E_{\beta J-1}$ is $\mp$

a_- represents the perturbation by the levels $\beta, J-1$ due to the operator $[\mathcal{E}\{P^{-1}\}] = [\mathcal{E} e r \cos\theta]$ on the level αJ. The square of the matrix element is divided by the difference in energy and summed over all the β values.

a_+ and a_0 are similar expressions giving the perturbation due to $\beta, J+1$ and β, J levels respectively.

The relative strength of the lines can also be calculated. Cf C & Shortley. [C+S p. 411]

Certain general conclusions may also be drawn about the appearance of certain forbidden lines when an electric field is applied.

The initial state is characterized by numbers $\alpha J M$ and has a certain parity say odd (S & d States). The states that perturb it are the $\beta J' M'$ states where $J' = J$ or $J \pm 1$ & $M' = M$ or $M \pm 1$. and further it has polarity opposite to that of the $\alpha J M$ state (p & f states) Now transitions from $\alpha J M$ state are allowed only to p, f states & transitions from $\alpha J M$ to any of the S, d states is forbidden. Similarly transitions from $\beta J' M$ to any even state is forbidden.

lines ($\beta J'M$ to ~~odd~~ even states)

Some of these ~~states~~ may however occur when the initial βJM is no more the original unperturbed state but one obtained by Stark effect perturbation.

The general expression for the perturbed eigenfunction in non-degenerate case is

$$\psi_n = \psi_n^\circ + \sum_s a_s \psi_s^\circ \quad \text{where} \quad \begin{matrix} n = (\beta J' M) \\ s = (\alpha J M) \end{matrix} \quad \text{only odd states}$$

$$a_s = \frac{L_{ns}}{E_n^\circ - E_s^\circ}$$

Thus we have $\psi(\beta J'M) = \psi_0(\beta J'M) + -\mathcal{E}\sum_\alpha \frac{(\beta J'\{P\}\alpha J'-1)\sqrt{J^2-m^2}}{E_{\beta J'} - E_{\alpha J'-1}} \psi_0(\alpha J'-1, M)$

$$-\mathcal{E}\sum_\alpha \frac{(\beta J'\{P\}\alpha J')M}{E_{\beta J'} - E_{\alpha J'}} \psi_0(\alpha J'M)$$

$$-\mathcal{E}\sum_\alpha \frac{(\beta J'\{P\}\alpha J'+1)\sqrt{(J'+1)^2-M^2}}{E_{\beta J'} - E_{\alpha J'+1}} \psi_0(\alpha J'+1, M)$$

Let $JJ''M''$ be the final state and assume that its perturbation ~~by~~ due to Stark Effect is negligible. If it has the same parity (even parity) as the $(\beta J'M)$ state its matrix component for dipole transition with $\psi_0(\beta J'M)$ vanishes. But the matrix component with $\psi(\beta J'M)$ does not vanish since there are three additional terms.

The matrix component is

$$(JJ''M''|\mathbf{P}|\beta J'M') = -\mathcal{E}\left\{\sum_\alpha \frac{(JJ''M''|\mathbf{P}|\alpha J'-1, M)(\beta J'\{P\}\alpha J'-1)\sqrt{J^2-M^2}}{E_{\beta J'} - E_{\alpha J'-1}}\right.$$

$$\left. + \text{two similar terms for } J' \text{ changes to } J'-n \text{ to } J'+1. \right\}$$

Weisskopf: Phys. Zeits. 34, n 1+, 1933

Natural line width $E = E_0 e^{-\gamma t}$; $\gamma = \frac{2}{3}\frac{e^2}{mc^3}\omega_0^2$

$$J(\omega) = \frac{\gamma}{2\pi}\cdot\frac{1}{(\omega-\omega_0)^2+\left(\frac{\gamma}{2}\right)^2}$$

ω is the frequency, not angular frequency.

Doppler line broadening $J(\omega) = C e^{-\frac{v_x^2}{\alpha^2}}$

$$\frac{\nu-\nu_0}{\nu_0} = \frac{v_x}{c} \quad \therefore dv_x = \frac{c}{\nu_0}d\nu \qquad J(\nu)d\nu = \frac{1}{\alpha\sqrt{\pi}}e^{-\frac{v_x^2}{\alpha^2}}dv_x$$

$$J(\nu)d\nu = \sqrt{\frac{m}{2kT\,\pi}}\cdot\frac{c}{\nu_0}\cdot e^{-\left(\frac{c}{\nu_0}\right)^2\cdot(\nu-\nu_0)^2\cdot\frac{1}{\alpha^2}}d\nu$$

Collision broadening Lorentz line shape.

$$J(\nu) = \text{Const.}\ \frac{1}{(\nu-\nu_0)^2+\left(\frac{1}{2\pi\tau}\right)^2} \quad ; \quad \frac{1}{\tau} = \pi\rho^2 n\,\bar{v} = 2\rho^2 n\alpha\cdot\sqrt{\pi}$$

Since ~~$\pi\bar{v} = 2\sqrt{\pi}\alpha$~~ $\bar{v} = \frac{2}{\sqrt{\pi}}\alpha$

Margenau P.R. 48, 755, 1935.

Assume $\Delta\nu = -\alpha \frac{1}{r^6}$ (1) so that terms in $\frac{1}{r^8}$ etc can be neglected.
Assume uniform distribution of perturbers.

$$I'(\nu)\,d\nu = \frac{4\pi}{V} r^2 dr$$ — if there is only one perturber.

The l.h.s. is probability of frequency ν in the broadened line and the r.h.s. is prob. of the perturber being at distance r

If there are n perturbers

$$I'(\nu)d\nu = \left(\frac{4\pi}{V}\right)^n \int\cdots\int_{d\nu} r_1^2 \cdot r_2^2 \cdots r_n^2 \cdot dr_1 \cdots dr_n \qquad (2)$$

where the integration extends over the range of r's in which

$$\nu - \frac{d\nu}{2} < -\sum_i \frac{\alpha}{r_i^6} < \nu + \frac{d\nu}{2} \qquad (3)$$

By inserting the Dirichlets factor which has value 1 in range (2) and vanishes outside,

$$I'(\nu)\,d\nu = \frac{1}{\pi}\left(\frac{4\pi}{V}\right)^n \int\cdots\int r_1^2 \cdots r_n^2\, dr_1 \cdots dr_n \cdot \int_{-\infty}^{\infty} d\rho \cdot \frac{\sin \frac{\rho\, d\nu}{2}}{\rho} \cdot e^{\left\{-i\nu\rho + i\alpha\rho \sum \frac{1}{r_i^6}\right\}}$$

which permits the r integrations to be taken over all accessible r space.

Assume $d\nu \to 0$ which simplifies the Sine factor. Then we split the integration over r's to write

$$e^{i\alpha\rho\frac{1}{r^6}} \text{ as } 1 - \left\{1 - e^{i\alpha\rho\frac{1}{r^6}}\right\}$$

$$\therefore I'(\nu)\,d\nu = \frac{1}{2\pi}\left(\frac{4\pi}{V}\right)^n \int_{-\infty}^{\infty} d\rho\, e^{i\nu\rho} \left[\int\left[1 - \left\{1 - e^{i\alpha\rho\frac{1}{r^6}}\right\}\right]\right]$$

$$I'(\nu) = \frac{1}{2\pi}\left(\frac{4\pi}{V}\right)^n \int_{-\infty}^{\infty} d\rho\, e^{-i\nu\rho} \left[\int\left\{1 - \left(1 - e^{i\alpha\rho\frac{1}{r^6}}\right)\right\} r^2 dr\right]^n \qquad (5)$$

Consider the term in [ ]. The integration is to be carried from some smallest distance of approach r, to the maximum distance of separation d, & d would be related to

the total volume by $\frac{4\pi d^3}{3} = V$. But in integrating $r^2 dr$ we are permitted without appreciable error to use zero as the lower limit & in integrating the remainder we may replace the upper limit by ∞ because of the behaviour of the integrand.

$$\int_0^\infty \left\{1 - \left(1 - e^{i\alpha\rho \frac{1}{r^6}}\right)\right\} r^2 dr = \left[\frac{V}{4\pi}\left\{1 - \frac{4\pi V'}{V}\right\}\right]$$

where $V' = \int_0^\infty \left(1 - e^{i\alpha\rho \frac{1}{r^6}}\right) r^2 dr$

In raising this quantity [ ] to the nth power we allow the volume of the gas to increase indefinitely while maintaining $n_1 = \frac{n}{V}$ constant.

Then $\lim_{n\to\infty} \left(1 - 4\pi n_1 \frac{V'}{n}\right)^n = e^{-4\pi n_1 V'}$

and (5) takes the form

$$\text{and } f(v') = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\rho \cdot e^{iv\rho} \cdot e^{-4\pi n_1 V'(\rho)} \qquad (6)$$

Now we proceed to evaluate $V'(\rho)$. Let $x = \frac{\alpha\rho}{r^6}$; by partial integration

$$V'(\rho) = \frac{\sqrt{\alpha\rho}}{3} \int_0^\infty \left(\frac{\sin x}{\sqrt{x}} - i\,\frac{\cos x}{\sqrt{x}}\right) dx = \frac{\sqrt{2\pi\alpha\rho}}{6}(1 - i).$$

When this is substituted into 6 there results an expression which is easily evaluated.

The integrand in (6) is changed to real form by writing

$$\int_{-\infty}^{\infty} = \int_0^\infty + \int_{-\infty}^0$$ & the variable in the second integration is taken to be $-\rho$ instead of ρ.

$$f'(v) = \frac{1}{\pi} \int_0^\infty e^{-\frac{2\pi}{3} n_1 \sqrt{2\pi\alpha\rho}} \cdot \cos\left(v\rho - \frac{2\pi}{3} n_1 \sqrt{2\pi\alpha\rho}\right) d\rho \qquad -(6\text{-}a)$$

This integral is of the form $\int_0^\infty e^{-px} \cos(x^2 - px)\, x\, dx$

with $x = \sqrt{v\rho}$.

$$\therefore f'(v) = \frac{2}{3}\pi\sqrt{\alpha} \cdot n_1 \cdot v^{-3/2} \cdot e^{-\frac{4}{9}\pi^3 \alpha n_1^2 \frac{1}{v}} \qquad (7)$$

Let $\lambda = \frac{2}{3}\pi\sqrt{\alpha} \cdot n_1$

Thus (7) becomes $f'(v) = \lambda v^{-3/2} \cdot e^{-\frac{\pi\lambda^2}{v}}$

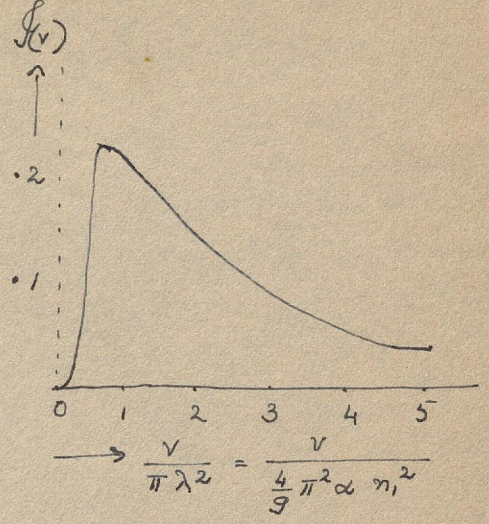
This expression is plotted in fig

The max. of (7) comes at

$$\nu_{max} = \frac{2}{3}\pi\lambda^2 = \left(\frac{2}{3}\pi\right)^3 \cdot \alpha n_1^2.$$

for single impacts

Kuhn's ~~*~~ Conclusion (Proc. Roy. Soc. A. 18 987, 1934) that for large ν the distribution should behave as $\nu^{-3/2}$ is borne out by eqn (7-a).



For small ν the exponential $e^{-\pi\lambda^2/\nu}$ is more significant. It represents the cooperation of several perturbers in producing the intensity at a given frequency.

The half-width is $1.85\pi\lambda^2 = 1.85 \cdot \left(\frac{2}{3}\pi n_1\right)^2 \alpha$.

which is proportional to the sq. of n_1.

Margenau and Watson : Pressure effects on Spectral lines

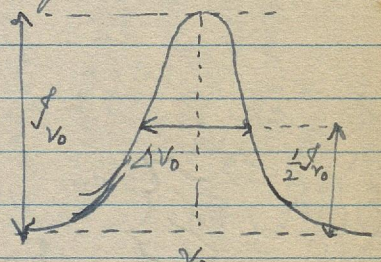
Rev. of Mod. Phys. 8, 22, 1936.

Causes producing width & Displacement of Spectral lines

The theories outlined below hold only for are valid for absorption lines - not for emission lines. It is assumed that the number of excited atoms is small and that therefore the interaction of excited states can be neglected. & We also assume that no external field is present.

Half-intensity width $\Delta\nu_{1/2}$ is defined by the eqn.

$$J_{(\nu_0 \pm \frac{1}{2}\Delta\nu_0)} = \frac{1}{2} J_{(\nu_0)}$$



A. Radiation Damping

A vibrating electric charge radiates energy. Hence the total energy decreases with time & thus the amplitude diminishes while frequency ν_0 remains constant. The frequency of the radiation is obtained by a Fourier analysis of $M(t)$ where M is the electric moment.

$$I(\nu) = \frac{\frac{\gamma}{2\pi}}{(\nu_0-\nu)^2 + \left(\frac{\gamma}{2}\right)^2} \quad \text{where } \gamma = \frac{4\pi}{3}\cdot\frac{e^2}{mc^3}\cdot\nu_0^2 \text{ sec}^{-1}$$

When $\nu = \nu_0$, I is max. $= I(\nu_0) = \frac{\gamma}{2\pi}\cdot\frac{4}{\gamma^2} = \frac{2}{\pi}\cdot\frac{1}{\gamma}$

When $(\nu_0 - \nu) = \pm\frac{\gamma}{2}$, I_x is $I(\nu_{1/2})$; i.e. the intensity is half max.

Half intensity width is γ

If γ is expressed in wavelength $\gamma = \frac{4\pi}{3}\frac{e^2}{mc}\frac{1}{\lambda_0^2}$

Intensity is $\frac{1}{2} I(\lambda)_{max}$ when $(\nu_0 - \nu) = \frac{\gamma}{2}$ i.e. $\frac{c}{\lambda_0} - \frac{c}{\lambda} = \frac{2\pi}{3}\frac{e^2}{mc}\frac{1}{\lambda_0^2}$

i.e. $\frac{\lambda-\lambda_0}{\lambda\lambda_0} = \frac{2\pi}{3}\frac{e^2}{mc^2}\frac{1}{\lambda_0^2}$ i.e. $\lambda - \lambda_0 = \frac{2\pi}{3}\frac{e^2}{mc^2}$ $\therefore \Delta\lambda = \frac{4\pi}{3}\frac{e^2}{mc^2}$.

$$\Delta\lambda = \frac{4\cdot2\times4\cdot8\times4\cdot8\times10^{-20}}{9\times10^{-28}\times9\times10^{20}} = 1\cdot17\times10^{-4} \text{ A.U.}$$

The half intensity width in wavelengths is seen to be independent of the λ_0 of the line.

This is contrary to observation.

In quantum mechanics, natural line width arises from the fact that the two energy levels E_1 & E_2 have a finite width as ΔE_1 & ΔE_2

The intensity distribution within the line is

$$I(\nu) = \frac{\gamma/2\pi}{(\nu_{21}-\nu)^2 + \left(\frac{\gamma}{2}\right)^2}$$

cf Weisskopf & Wigner Z. f. Phys 63, 54, 1930; 65, 18, 31

Hoyt P.R. 36, 860, 1930.

$\nu_{21} = \frac{E_2 - E_1}{h}$ & $\gamma = \gamma_1 + \gamma_2 = \frac{\Delta E_1}{h} + \frac{\Delta E_2}{h}$

If Δt_1 is the average time the atom remains in State E_1,

$$\Delta E_1 \cdot \Delta t_1 \sim \frac{h}{2\pi}$$

$\frac{1}{\Delta t_1}$ is the total number of spontaneous emissions p.s. that can occur when atom is in State E_1

If E_k is a lower state, the number of transitions p.s. from E_1 to E_k is $\frac{8\pi^2 e^2}{mc^3} \nu_{1k}^2 f_{1k}$ where f_{1k} is the "oscillator-strength" corresponding to transition from 1 to k.

$$\frac{1}{\Delta t_1} = \frac{8\pi^2 e^2}{mc^3} \sum \nu_{1k}^2 f_{1k} \quad \text{or} \quad \Delta E_1 = \frac{4\pi e^2 h}{mc^3} \sum \nu_{1k}^2 f_{1k}$$

$$\gamma = \frac{4\pi e^2}{mc^3} \left\{ \sum_k \nu_{1k}^2 f_{1k} + \sum_l \nu_{2l}^2 f_{2l} \right\}$$

In the particular case of Na resonance line, the lower state has no downward transitions $\therefore f_{1k} = 0$ & $f_{2k} = 1/3 \therefore \gamma = \frac{4\pi e^2 \nu^2}{3mc^3}$ which is the same as the one obtained classically.

B Doppler Effect

Let light of uniform intensity distribution shine through a gas. If the atoms were at rest they would absorb a nearly sharp frequency ν_0. Atoms having velocity v_x in the direction of propagation of the light will by the Doppler's principle absorb a frequency

$$\nu = \nu_0 \left(1 - \frac{v_x}{c}\right).$$

The fractional number of such atoms within the range dv_x is

$$\frac{dn}{n} = \frac{\sqrt{M}}{\sqrt{2\pi RT}} \cdot e^{-\frac{M}{2RT} v_x^2} dv_x$$

where M is the molecular weight of the gas

This formula also represents the fraction of the total intensity which is absorbed at a frequency $\nu = \nu_0 \left(1 - \frac{v_x}{c}\right)$.

$$f(\nu) = \left\{ \frac{Mc^2}{2\pi RT \nu_0^2} \right\}^{1/2} e^{-\left(\frac{Mc^2}{2RT\nu_0^2}\right)(\nu - \nu_0)^2}$$

Thus Doppler effect causes the atoms in the absorption or emission line to take on a Gaussian distribution

The half-width of the line is

$$\Delta\nu_{1/2} = 2\sqrt{\log 2} \cdot \sqrt{\frac{2RT}{Mc^2}} \cdot \nu_0$$

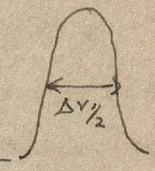
and on the wavelength scale

Outline of the theory of Holtzmark & Spitzer

Introduction

Natural line width - Classical theory $E = E_0 e^{-\gamma t}$

$$f(\nu) = \frac{\gamma}{2\pi} \frac{1}{(\nu-\nu_0)^2 + (\frac{\gamma}{2})^2} \quad ; \quad \int_{-\infty}^{\infty} f(\nu)\, d\nu = 1.$$



$\Delta\nu_{1/2} = \gamma = \frac{4\pi}{3} \frac{e^2}{mc^3} \nu_0^2$; $\Delta\lambda_{1/2} = .00012$ A.U. nearly

$\Delta\lambda_{1/2}$ is independent of wavelength.

Quantum theory gives the dependance on wavelength. Number of transitions p.s. from state E_i to state of energy E_i to state of energy E_k $(E_k < E_i)$ is $\frac{1}{\Delta t_i} = \frac{8\pi^2 e^2}{mc^3} \nu_{ik}^2 \cdot f_{ik}$ & Since $\Delta E_i \cdot \Delta t_i = \frac{h}{2\pi}$

$$\gamma = \frac{4\pi e^2}{mc^3} \left\{ \sum_k \nu_{ik}^2 f_{ik} + \sum \nu_{2l}^2 \cdot f_{2l} \right\}$$ which

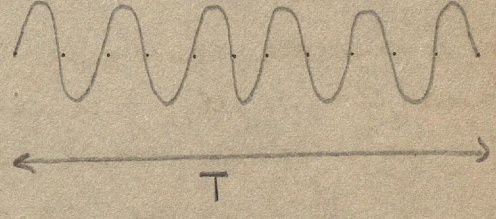
In the case of D_1, D_2 lines, $f_{ik} = \frac{1}{3}$ & $f_{2l} = 0$ $\therefore$ $\gamma = \frac{4\pi}{3} \frac{e^2}{mc^3} \nu_0^2$ which is the same as the classical value.

Doppler effect $\frac{\nu - \nu_0}{\nu_0} = \frac{v_x}{c}$ $\therefore$ $f(\nu) = \frac{1}{\alpha\sqrt{\pi}} \frac{c}{\nu_0} e^{-\frac{1}{\alpha^2}\left\{\frac{c}{\nu_0}(\nu-\nu_0)\right\}^2}$

$\alpha = \sqrt{\frac{2kT}{m}}$; $\Delta\nu_{1/2} = 2\sqrt{\log 2} \cdot \frac{\alpha}{c} \nu_0$

Doppler line width is about the same as natural line width at 100 A.U. In the visible region it is 50 times greater.

Lorentz line shape



Based on the assumption that the frequency ν_0 and the amplitude remain constant for time interval T between successive collisions and that each collision is a collision of the second kind.

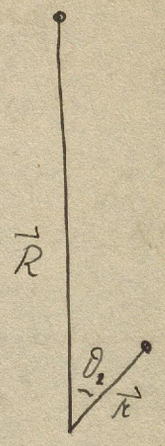
$$f(\nu) = \frac{1}{2\pi^2 \bar{T}} \int_0^{\infty} \frac{\sin^2 \pi(\nu-\nu_0)T}{\{\pi(\nu-\nu_0)\}^2} e^{-T/\bar{T}}\, dT = \frac{1}{2\pi^2 \bar{T}} \frac{1}{(\nu-\nu_0)^2 + \left(\frac{1}{2\pi\bar{T}}\right)^2}$$

$\frac{1}{\bar{T}} = \pi \rho^2 \bar{v} n$. $\therefore$ $\Delta\nu_{1/2} = \rho^2 \bar{v} n$.

That the half intensity width is proportional to n has been verified, but values of ρ are not consistent; for D_1, D_2 of Na is broadened by N_2, ρ varies between 2 & 12 A.U.

Holtzmark Theory

$\vec{F} \cdot \vec{r} = \frac{r}{R^p} w_p$ where $p = 2, 3,$ or 4 gives the scalar potential at $\vec{r}$ due to an ion, dipole or quadrupole at $\vec{R}$.



We assume a random distribution of the charged particles & that all particles are of the same kind.

For $p = 2$, (ion) $w_p = -e \cos\theta_2$.

w_3 & w_4 involve $\theta_1, \theta_2, \varphi_1, \varphi_2$ which define the directions of $\vec{R}$ & $\vec{r}$.

Let $\vec{F}_0$ be a given value for the resultant field at the atom due to N charges randomly distributed. We wish to find the probability of $\sum_{i=1}^{N} \frac{r}{R_i^p} w_{p_i}$ lying in the region $\left[\vec{F}_0 \cdot \vec{r} + \frac{1}{2}\Delta(\vec{F}_0 \cdot \vec{r})\right]$ to $\left[\vec{F}_0 \cdot \vec{r} - \frac{1}{2}\Delta(\vec{F}_0 \cdot \vec{r})\right]$

$$P\left\{\left[\vec{F}_0 \cdot \vec{r} + \tfrac{1}{2}\Delta(\vec{F}_0 \cdot \vec{r})\right] > \sum_{i=1}^{N} \frac{r}{R_i^p} w_{p_i} > \left[\vec{F}_0 \cdot \vec{r} - \tfrac{1}{2}\Delta(\vec{F}_0 \cdot \vec{r})\right]\right\} \quad (1)$$

$$= W(\vec{F}_0) = \frac{1}{(2\pi)^3} \iiint d\xi\, d\eta\, d\zeta\, e^{-i(\vec{F}_0 \cdot \vec{r})} \cdot f^N$$

where $f = \frac{1}{\left(\frac{4}{3}\pi R_{max}^3 \cdot 4\pi\right)} \cdot \underbrace{\iiint}_{B} e^{i \frac{r}{R^p} w_p} \cdot \underbrace{(dR\, R d\theta_1 \cdot R \sin\theta_1 d\varphi_1 \cdot d\theta_2 \sin\theta_2 d\varphi_2)}_{A} \quad (2)$

ξ, η, ζ are the Cartesian coordinates of $\vec{r}$. The expression $(dR \ldots d\varphi_2)$ is an element of volume dV'; & $\left(\frac{4}{3}\pi R_{max}^3 4\pi\right)$ is the total volume V'

$\frac{dV'}{V'}$ is the probability of finding the charge in a given position, & the electron in a given direction relative to charge

$\prod_{i=1}^{i=N} \frac{dV^i}{V^i}$ is the probability of finding each charge in given position & the electron in given relative direction with respect to the charge.

Integrating the i product term for all values of R_i & w_i which satisfy eqn (1) we obtain the probability $W(\vec{F}_0)\, d\vec{F}_0$.

Now $d\vec{F}_0 \cdot \frac{1}{(2\pi)^3} \iiint d\xi\, d\eta\, d\zeta \cdot e^{i\left(\sum \frac{r}{R_{pi}} \omega_{pi} - \vec{F}_0 \cdot \vec{r}\right)}$ has value 1 in the range of ① and is zero outside.

Thus
$$W(\vec{F}_0)\, d\vec{F}_0 = \int_{5N} \cdots \int \prod_i^N \frac{dV_i}{V_i} \cdot \frac{d\vec{F}_0}{(2\pi)^3} \iiint d\xi\, d\eta\, d\zeta\, e^{i\left\{\sum \frac{r}{R_i^p} \omega_{pi} - \vec{F}_0 \cdot \vec{r}\right\}}$$

in which the integral for V can be extended to the whole domain. By separation of variables we get eqn (2). Define $n = \frac{N}{V}$

$$J_2^N = e^{-C_2 r^{3/2}} \qquad \text{where } F_n = C_2 = 2.61\, n^{2/3} e^{2/3}.$$

$$J_3^N = e^{-C_3 r} \qquad \text{where } F_n = C_3 = 4.54\, n \cdot \mu \quad \text{(graphical method)}$$

$$J_4^N = e^{-C_4 r^{3/4}} \qquad \text{where } F_n = C_4^{4/3} = 25.67\, n^{4/3} \cdot A \quad \text{(graphical method)}$$

Define $\beta = \frac{F_0}{F_n}$; $W(F_0) = W(\vec{F}_0) \cdot 4\pi F_0^2$. Set $v = (F_0 r)^{3/2}$

For coins
$$W(\vec{F}_0) = \frac{1}{2\pi^2} \cdot \frac{2}{3} \cdot \frac{1}{F_0^3} \int_0^\infty e^{-C_2 v / F_0^{3/2}} \cdot v^{1/3} \sin v^{2/3}\, dv \quad \text{or in another form}$$

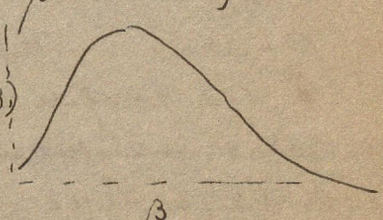
$$W(F_0) = \frac{H(\beta)}{F_n} \quad \text{where } H(\beta) = \frac{2}{\pi\beta} \int_0^\infty e^{-(x/\beta)^{3/2}} \cdot x \cdot \sin x \cdot dx.$$

For x large The integration can be performed by expanding the exponential function or the sine function in powers of the variable x or v. The result is obtained as a series of M functions.

For β small, $W(F_0)\, dF_0 = d\beta \cdot \frac{4\beta^2}{3\pi} \left\{ 1 - \cdot 4\beta^2 + \cdot 1\beta^4 - \cdot 02\beta^6 \ldots \right\}$

β large $W(F_0)\, dF_0 = d\beta \cdot \frac{2 \cdot 30}{\pi \beta^{5/2}} \left\{ 1 + \frac{5}{\beta^{3/2}} - \frac{7}{\beta^{6/2}} + \ldots \right\}$

In the region β between 3.4 & 4.4 both the series ~~are divergent~~ converge too slowly.



Main application of this theory is to the gravitational field at a point in space due to a random distribution of stars. Observe however that distances are 10^{12} miles (3 parsecs) & masses are 10^{32} gms.

For large values of F_0 the probability function

of the field due solely to the nearest star is practically the same as that due all stars randomly distributed.

One defect in theory is that all positions are assumed equally probable & ∴ integration for R is taken down to R = 0. But when two stars get too close they form a binary system. The Holtzmark distribution has too long a tail; its second moment ~~does not vanish~~ does not exist.

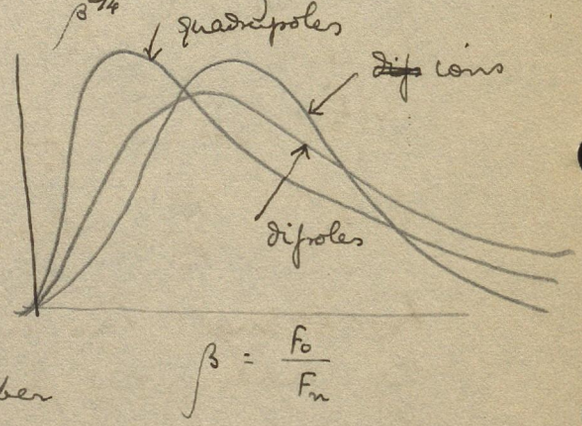
Dipoles: $W(F_0)\,dF_0 = d\beta \cdot \frac{4}{\pi}\frac{\beta^2}{(1+\beta^2)^2}$.

Quadrupoles For $\beta < 1$ graphical method gives

$$W(F_0)\,dF_0 = \frac{4}{3}\frac{4}{\pi}\cdot\beta^2 d\beta\left\{1 - 2\beta^2 + 11\beta^4 \ldots\right\}$$

& for large β

$$W(F_0)\,dF_0 = \frac{4}{\pi}d\beta \cdot \frac{1}{\beta^{7/4}} \times 0.805\left\{1 - \frac{7}{\beta^{3/4}} + \ldots\right\}$$

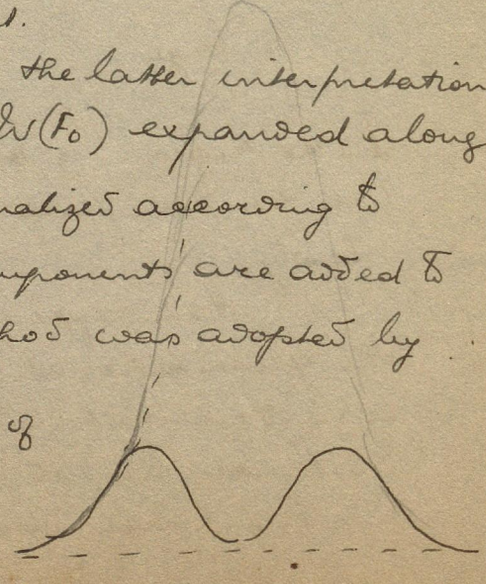


The ordinate of the W & β curve for any given value of F_0 can be interpreted as the amount of time the atom is subjected to that value of the field. Or if the changes in field take place very slowly (high n or low α) the ordinate of the curve gives the number of atoms which are subject to that value of field.

For any given Stark effect component of a hydrogen line, $(\nu - \nu_0) = C_r F_0$ where C is a constant for that component.

Hence the profile of the line under the latter interpretation of $W(F_0)$ is the same as the profile of $W(F_0)$ expanded along the x-axis in the ratio $C_r : 1$

The profile of each component is normalized according to its relative intensity & the profiles of all components are added to give the profile of the whole line. This method was adopted by Craggs & Hopwood & earlier by Verweij.



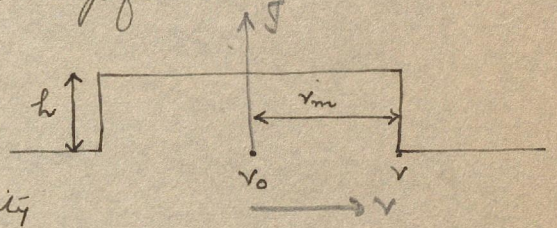
Craggs & Hopwood determined the value of F_n for which the theoretical curve would agree most closely with the experimental

Curve A since $F_n = 2.61 \times n^{2/3} \times e$, the value of n is Calculated. The ~~observed~~ experimental curve agrees with the theoretical one for only a small portion of the wing of the line.

Holtzmark's method of calculating the line profile was by ~~setting~~ approximating the profile of the line under a constant field F' to be given by a step function

$2\nu_m = 2(\nu - \nu_0) = C F'$

Where ν is the frequency of the outermost component.



$h \times 2\nu_m = f$ the total intensity

$$J(\nu)d\nu = d\nu \int_{F'}^{\infty} \frac{f}{2\nu_m} \cdot W(F)dF \qquad (4)$$

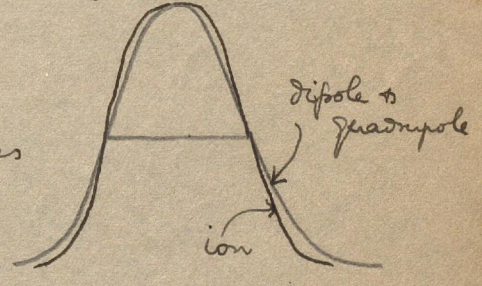
where F' is the field just sufficient to displace the outermost component of from ν_0 to ν.

The curve of eqn (4) was Calculated graphically for the three cases. The values of half intensity width are

$\Delta\nu_{1/2} = 3.25\ C\ n^{2/3} \cdot e$ ions

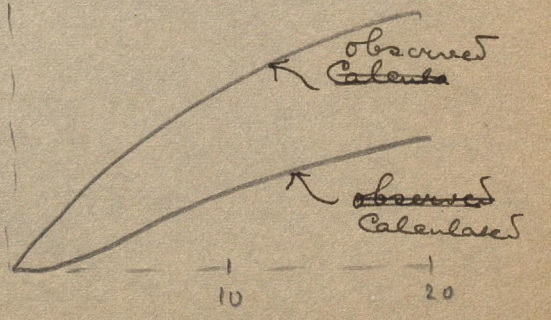
$= 4.54\ C\ n \cdot \mu$ dipoles

$= 17.2\ C\ n^{4/3}\ A$ quadrupoles.



Holtzmark applies the theory to the broadening of H_α line which was assumed to be due to the quadrupole moment of H_2 molecule. $\Delta\nu_{1/2}$ was measured for pressure 1 mm to 20 cm of Hg. A was assumed to be 3.2×10^{-26}, a value which is now known to be too large.

Observed values were ~~20~~ 100% or more higher.



$$\Delta\lambda_{1/2} = 2\sqrt{\log 2}\,\sqrt{\frac{2RT}{Mc^2}}\,\lambda_0$$

Thus on the wavelength scale the natural line-width is approximately independent of the wavelength while the Doppler line-width increases with wavelength. The two effects are nearly equal at $\lambda = 100°$ A.U. & in the optical region the natural line width is masked by the Doppler broadening. But the Gaussian curve falls off more rapidly than that of natural line width & hence for large $(\nu - \nu_0)$ the natural line width is more significant Cf Weisskopf Phys. Zeits 34, 1, 1933.

Both these effects are independent of the density of the gas.

C Resonance between Similar atoms.

Assume all atoms of the monatomic gas to be dipoles, each having frequency ν_0. If there is no coupling forces between dipoles, each oscillator can absorb only frequency ν_0 from the incident radiation.

Since the dipoles exert forces on each other, the assemblage of a dipoles forms a coupled system. The force of coupling is $F_{ij} = \frac{\text{Const}}{r_{ij}^4}$ where r_{ij} is the distance of the jth dipole from the ith one.

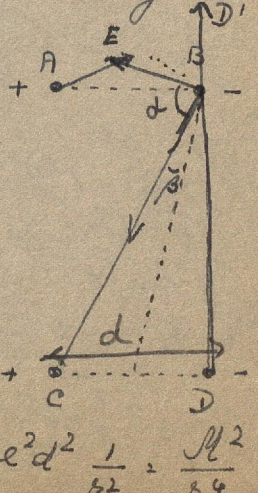
Hence the system he has in addition to ν_0 a large number of other natural frequencies distributed around ν_0. If there is no thermal motion these frequencies would be discrete; actually they merge into one another and form a continuum.

This gives rise to what is called the broadening due to coupling.

Note: To show that $F_{ij} = \frac{C}{r_{ij}^4}$

Force of C & D on B is resultant of $\frac{e^2}{r^2}$ along BD' & $\frac{e^2}{r^2}$ along BC

$= \frac{2e^2}{r^2}\cdot\cos\alpha = \frac{2e^2}{r^2}\sin\beta = \frac{2e^2}{r^2}\beta.$

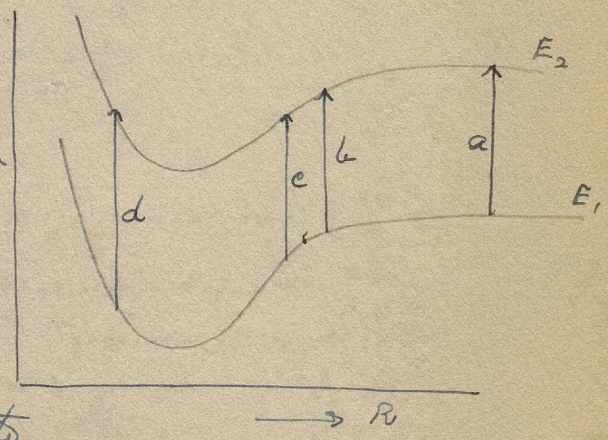


Force of C & D on A & B = resultant of $\frac{2e^2}{r^2}\beta$ along BE & an equal force along AE $= 2\cdot\frac{2e^2}{r^2}\beta\cdot\sin\beta = \frac{4e^2}{r^2}\beta^2 = 4e^2\frac{d^2}{4}\frac{1}{r^4} = e^2d^2\frac{1}{r^2}\cdot\frac{M^2}{r^4}$

But atoms which are in normal states have a symmetrical charge distribution and are not permanent dipoles. Abroad The broadening usually called that due to Coupling is really due to optical resonance Since between an excited atom and a normal atom there exists a force which varies as $1/R^4$.

1) Broadening due to forces of the Van der Waals type:

When the absorbing atom is surrounded by atoms of a different kind, (say Na by A) the energy levels of Na are modified A qualitative description may be given by the aid of potential energy curves E_1, E_2. In the absence of the perturber, the curves are st. lines; as perturber comes closer, i.e. R decreases, the levels first are lowered. The effect on the upper level is greater than on the lower level. Hence transition $c < b < a$. The absorbed frequency as ν is $< \nu_0$ where $\nu_0 = \frac{a}{h}$, & $\nu = \frac{c}{h}$.



Very close encounters correspond to transition d; but such encounters are relatively few.

The effect is on an average one of broadening with red Shift.

E. Broadening by foreign perturbers carrying permanent fields.

The fields may be due to poles, dipoles or quadrupoles.

Holtsmark and Debye (Ann. Phys. 58, 577, 1919) & Debye (Phys. Zeit 20, 160, 1919) Calculated the line width with the following assumptions

1) The broadening is due to a displacement of the energy levels due to Stark effect

2) The effective field strength is that produced by the perturber at the centre of the atom.

3) The fields vary infinitely slowly compared with the time of emission or absorption.

Holtzmark evaluated the intensity distribution by the graphical method. He showed that the line width is

$$\Delta\nu_{1/2} = \text{Const.}\ n_1^{2/3}$$

where n_1 is the number of perturbers per unit volume.

§3 General Methods of Calculating intensity distribution

The frequency of the absorbing or emitting atom is disturbed by external influences; and these influences vary with time.

The classical treatment is as follows:

The active atom is treated as an oscillator of natural frequency ν_0. Because of external effects this frequency is changed from ν_0 to ν or $\nu = \nu(t)$

$$\nu = \nu_0 + \Delta\nu(t).$$

And the amplitude A_0 changes to $A(t)$.

Hence the electric moment at any instant t is

$$M(t) = A(t)\, e^{2\pi i \int_0^t \nu(\tau)\, d\tau}$$

The electric moment $M(t)$ of the oscillator and the amplitude $J(\nu')$ of the radiation are related by the Fourier integrals

$$M(t) = \int_{-\infty}^{\infty} J(\nu')\, e^{2\pi i \nu' t}\, d\nu' \quad \text{or} \quad J(\nu') = \int_{-\infty}^{\infty} M(t)\, e^{-2\pi i \nu' t}\, dt.$$

Hence
$$J(\nu') = \int_{-\infty}^{\infty} A(t)\, e^{2\pi i \left\{ \int_0^t \nu(\tau)\, d\tau - \nu' t \right\}} dt \qquad (3\text{-}4)$$

and the intensity $I(\nu') = |J(\nu')|^2$.

Under certain simplifying assumptions the quantum-mechanical treatment gives for $J(\nu')$ the same eqn as (3-4). Thus Lenz (Zeits Phys. 25, 299, 1924) proved (3-4) by invoking the correspondence principle and Weisskopf (Zeit Phys 75, 287, 1932) by using the K. W. B. approximation.

Mauguenau & Beatson give a simpler proof assuming that the external influence leaves A unchanged, but changes the frequency $A(t) = A_0$; $\int_0^t \nu(\tau)\, d\tau \neq \nu_0 t$. This is equivalent in the classical problem to assuming that the charge distribution is unchanged but the total energy of the oscillator is altered.

$$\mathcal{H}_0 \psi_0 = +\frac{h}{i}\frac{\partial}{\partial t}\psi_0 \quad \text{or} \quad (\mathcal{H}_0 + \mathcal{L})\psi = +\frac{h}{i}\frac{\partial}{\partial t}\psi.$$

Assume $(\mathcal{H}_0 + \mathcal{L}(t))\psi = (E_0 + \varepsilon(t))\psi$ or $\psi_0 = u_0 e^{+\frac{i}{h} E_0 t}$

or $\psi = u_0\, e^{+\frac{i}{h}\{E_0 + \varepsilon(t)\}t}$. This last eqn is justified since $\mathcal{L}$ does not change u_0.

The solution for $(\mathcal{H}_0 + \mathcal{L})\psi = +\frac{h}{i}\frac{\partial}{\partial t}\psi$ is $\psi = u_0 e^{+\frac{i}{h}\int_0^t \{E_0 + \varepsilon(t)\}\, d\tau}$ as may be proved by direct differentiation.

In this eqn ψ is to be identified as the probability amplitude at time t of the oscillator i.e. $\psi = A(t)$.

a_0 is the ~~space~~ probability amplitude at time $t = 0$ & since $A(t)$ is assumed to be constant in time, $a_0 = A(t)$.

$$\therefore E_0 + \varepsilon(t) = h\nu_0 + \Delta V(t) = h\nu$$

$$\text{so that } \frac{i}{\hbar}\int_0^t \{E_0 + \varepsilon(t)\}\,d\tau = 2\pi i \int_0^t \nu(t)\,d\tau.$$

Thus the classical value of the electric moment is the solution for the time-dependent Schroedinger eqn:

$$E_0 + \varepsilon(t) = \{E_{02} + \varepsilon_2(t)\} - \{E_{01} + \varepsilon_1(t)\}$$

where the ~~superscripts~~ subscripts 1 & 2 refer to the upper & lower states.

§ 4 Van der Waals' Interaction.

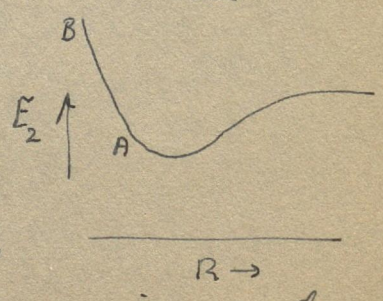
Given a single perturber in state l acting on the radiating or absorbing atom in state k, & if the two atoms are of different kinds, change in energy of the state k is according to F. London

$$\Delta\varepsilon'_{kl} = -\frac{1}{R^6}\,\frac{3}{2m^2}\left(\frac{he}{2\pi}\right)^4 \sum_{k'l'} \frac{f_{kk'}\cdot f_{ll'}}{(E_{k'} - E_k)(F_{l'} - F_l)(E_{k'} + F_{l'} - E_k - F_l)} + S. \quad (4-1)$$

S contains terms in $\frac{1}{R^8}$ etc. $f_{kk'}$ is the oscillator strength for transitions $k \to k'$ in the ~~first atom~~ "k" atom. Summation is over all $k' \neq k$.

The multiplicity of the Stark effect splitting which is due to the atom being differently oriented w.r.t. the perturbing ~~atom~~ field has been ignored in this eqn (4-1). The different levels are being replaced by a sharp average.

Terms in S become appreciable when $R \sim$ 10 A.U. When $R \sim 5$ A.U. for then exchange forces of the valence type set in and cause strong repulsion, corresponding to portion AB of the energy level curve or can result in chemical coalescence



Eqn (4-1) may be written $\Delta\varepsilon'_{kl} = -C_4\frac{1}{R^6}$ ~~$\Delta E_2 \sim -Q\frac{1}{R^6}$~~

~~If~~ Since more than one perturber acts on the atom, & the frequency emitted absorbed depends on ΔE of both upper ~~$\Delta E_2 \sim -Q\sum\frac{1}{R_i^6}$~~ and lower levels

$$\varepsilon = E_2 - E_1 + a\sum\frac{1}{R_i^6} \quad \& \quad \nu = \nu_0 + b\sum\frac{1}{R_i^6}$$

Resonance Interaction

Given only two atoms, say of Na, both in the normal state, given that the atoms are in equilibrium with continuous radiation, corresponding to 5890 or 5896, the atom will absorb only 5890 if the upper & lower states are in no way perturbed by the influence of the other Na atom. Actually the near presence of the other atom changes the upper energy level from ν_0 to

$$\nu = \nu_0 \pm B \frac{1}{R^3} \qquad \text{where } B = \frac{e^2}{8\pi^2 m \nu_0} \cdot \gamma \cdot f_{12}$$

where $\gamma = -2$ if $m = 0$ & $\gamma = +1$ if $m = \pm 1$ (m: magnetic quantum number)

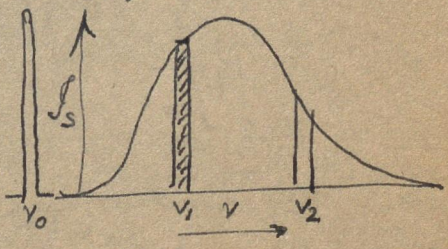
True distribution: Statistical distribution & Velocity distribution

Let the emitting atom be subjected to a constant field. The levels undergo Stark effect splitting. A single line splits into a large number of components of varying intensities.

Let the external field be that due to a foreign atom at distance R. According to our simple treatment of the problem, the levels are both depressed (in most cases) and the line shifts to a new position ν_0 changes to $\nu = \nu_0 + b \frac{1}{R^6}$.

Actually there are perturbing atoms at different values of R and the total effect of all of them is a distribution of ν values around a certain mean ν. This distribution can be calculated by methods of Statistical mechanics, and may be called Statistical distribution. This tells us what modified frequencies are actually possible for the perturbed system.

Imagine now an ideal case of a system having different oscillators, with frequencies distributed as given by the statistical distribution. Thus the number of oscillators emitting frequencies in the range $(\nu_1, \nu_1 + \Delta\nu_1)$ is equal to the area $I_S(\nu_1)\,\Delta\nu_1$. And each oscillator is assumed to emit radiation for an infinitely long interval of time.



Hence the natural half-width of the ~~radiation~~ emitted lines would be infinitely small and the ~~act~~ ~~Dis~~ true distribution of frequencies in the emitted radiation will be ~~equal to the~~ the same as the Statistical distribution.

Actually an ~~system~~ atom emitting a perturbed frequency ν does so only for a finite interval of time Δt after which it moves to another distance $(R + \Delta R)$ from the perturber and hence emits a different frequency $\nu + \Delta\nu$. The wave train corresponding to frequency ν is of finite length and hence ~~it~~ has a frequency spread $\Delta\nu$ about the mean value ν. The frequency spread is calculated in the same ~~fas~~ manner as the natural line breadth. ~~It~~ Since this is due to the atoms having a finite, non-zero velocity may be called a velocity distribution. The velocity distribution is superposed on the Statistical distribution. The velocity distribution is of the order of $\frac{kT}{h}$ and increases with temperature.

If $J(\nu')$ is the amplitude corresponding to any frequency ν' in the emitted radiation and $\nu(\tau)$ is the frequency of the emitter at time t,

$$J(\nu') = \int_{t=-\infty}^{\infty} A(t)\, e^{2\pi i\left[\left\{\int_{\tau=0}^{t} \nu(\tau)\, d\tau\right\} - \nu' t\right]} dt$$

The corresponding intensity is $|J(\nu')|^2$ i.e. ~~$J(\nu') \cdot J(\nu')$~~. Setting $A(t) = 1$

$$J(\nu') = \int_{t_1=-\infty}^{\infty} \left\{ \int_{t_2=-\infty}^{\infty} e^{2\pi i\left\{\int_0^{t_1} \nu(\tau)\, d\tau - \int_0^{t_2} \nu(\tau)\, d\tau - \nu' t_1 + \nu' t_2\right\}} dt_2 \right\} dt_1$$

in which setting $t_2 - t_1 = x$

$$J(\nu') = \int_{t_1=-\infty}^{\infty} \left\{ \int_{-\infty}^{\infty} e^{2\pi i\left\{\nu' x - \int_0^{x} \nu(\tau)\, d\tau\right\}} dx. \right\} dt_1$$

dt_1 has to be identified as $f_s(\nu)\, d\nu$

viz the statistical distribution of frequency ν in the oscillating System. The integral over x is the velocity distribution of ν' about ν.

If the velocity is so small that $\int_0^{x} \nu(\tau)\, d\tau = \nu(t) \cdot x$

$J(\nu')$ reduces to a simple form

$$J(\nu') = \int_{-\infty}^{\infty} \left\{ \int_{-\infty}^{\infty} e^{2\pi i[\nu' - \nu(t_1)]x} dx \right\} dt_1 = \lim_{a\to\infty} \int_{-\infty}^{\infty} \frac{\sin 2\pi a[\nu' - \nu(t_1)]}{\pi[\nu' - \nu(t_1)]} dt_1$$

$$= \lim_{a\to\infty} \int_{-\infty}^{\infty} \frac{\sin 2\pi a[\nu' - \nu(t_1)]}{\pi[\nu' - \nu(t_1)]} J_s(\nu)\, d\nu$$

In general $\int_0^x \nu(\tau)\, d\tau \neq \nu(t_1)\cdot x$ and hence $J(\nu')$ has to be written in the general form

$$J(\nu') = \int J_s(\nu)\, F(\nu'\nu)\, d\nu$$

in terms of J_s the Statistical distribution and F the velocity distribution.

Impact Theories – Lorentz line shape.

If each collision stops the radiation process completely, & T is the time interval between successive collisions,

$$J(\nu') = \text{Const.} \int_{-T/2}^{T/2} e^{2\pi i(\nu_0 - \nu')t} dt = \text{Const.} \frac{\sin \pi(\nu_0 - \nu')T}{\pi(\nu_0 - \nu')}$$

$$I(\nu') = \{J(\nu')\}^2.$$

But T is not the same for all collisions. Hence we have to average $I(\nu')$ over all collisions.

Probability that collision time lies in $(T, T+dT)$ is proportional to $e^{-\frac{T}{\bar{T}}} dT$

where $\bar{T}$ is the average time between collisions.

$$\overline{I(\nu')} = \text{Const} \int_0^{\infty} \frac{\sin^2 \pi(\nu_0 - \nu')T}{\pi^2(\nu_0 - \nu')^2} e^{-\frac{T}{\bar{T}}} dT = \frac{\text{Const}}{(\nu' - \nu_0)^2 + \left(\frac{1}{2\pi\bar{T}}\right)^2}$$

The half width of this curve called the Lorentz curve is

$$\Delta\nu_{1/2} = \frac{1}{\pi\bar{T}}.$$

If the classical mechanism of radiation damping is included in the derivation the expression is unaltered except that $\frac{1}{2\pi\bar{T}} + \frac{\gamma}{4\pi^2}$ has to be written for $\frac{1}{\pi\bar{T}}$.

Since $\frac{1}{\tau}$ is the number of collisions p.s. $\pi = \pi \rho^2 \bar{v} n$,

where $\Delta\nu_{1/2} = \rho^2 \bar{v} n$,

Here ρ is the optical collision diameter, the distance required so that the radiative process may stop.

Weisskopff Theory - Margenau's Theory of Lent.

Holtsmark Ann. d. Phys. 58, 577, 1919.

The central problem in Holtsmark's analysis is to determine the probability distribution function $W(F)$, viz the probability that the resultant field at a point has an absolute value between F and $F+dF$ when the field is due to a random distribution of ~~charged particles. The parti~~ ions, dipoles or quadrupoles.

First we consider the scalar function $\vec{F}.\vec{r}$ where $\vec{F}$ is the field and $\vec{r}$ the distance of the electron from the centre of the atom. $\vec{F}$ is assumed to be uniform for all $\vec{r}$.

If the field is due to a single ion

$$\vec{F}.\vec{r} = -\frac{e}{R^2} r\cos\theta. = \frac{r}{R^2} w_2 \quad \text{where } w_2 = -e\cos\theta$$

If ~~the~~ $\vec{F}$ is due to a dipole

$$\vec{F}.\vec{r} = \frac{r}{R^3} w_3 \quad \text{where } w_3 = w_3(\mu, \theta_1, \theta_2, \varphi_1, \varphi_2)$$

If $\vec{F}$ is due to a quadrupole

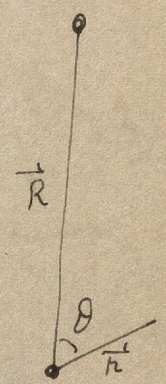
$$\vec{F}.\vec{s} = \frac{r}{R^4} w_4 \quad \text{where } w_4 = w_4(A, \theta_1, \theta_2, \varphi_1, \varphi_2)$$

Thus for all three cases

$$\vec{F}.\vec{r} = \frac{r}{R^p} w_p \quad \text{where } p = 2, 3, 4.$$

Let $\vec{F}_0 = \sum_1^N \vec{F}_i$ where N is the total number of particles.

In order to ~~g~~ derive the integral form for $W(\vec{F}_0)$, we consider the simpler case of forces of the Van der Waal's type.



$$\nu - \nu_0 = C\frac{1}{R^6} \quad \text{where } C \text{ is a constant.}$$

and if there are N atoms $\nu - \nu_0 = C\sum \frac{1}{R_i^6}$.

If there is only one perturber, the probability $W(\nu)$ of the frequency shift ~~ν~~ being between $(\nu-\nu_0)$ & $(\nu+\delta\nu-\nu_0)$ is probability of the perturber being at distance R, viz

$$f(\nu)d\nu = \frac{1}{V} 4\pi R^2 dR.$$

If there are N perturbers

$$\text{※}\quad J(\nu)\,d\nu = \left(\frac{4\pi}{V}\right)^N \cdot \int\cdots\int_{\Delta V} R_1^2 R_2^2 \cdots R_n^2\, dR_1 \cdots dR_n \qquad (1)$$

integrated over ΔV such that

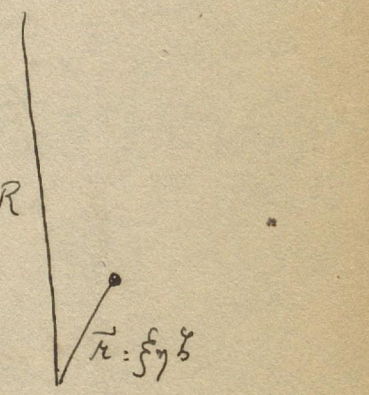
$$\left[\left(\nu - \frac{\delta\nu}{2}\right) - \nu_0\right] < C\sum \frac{1}{R_i^6} < \left[\left(\nu + \frac{\delta\nu}{2}\right) - \nu_0\right] \qquad (2)$$

The integration is performed by introducing the Dirichlet function which is 1 over the domain defined by (2) and zero elsewhere.

cf Mayenau P. R. 48, 755, 1935.

Here we have

$$W(\vec{F}_0) = \frac{1}{8\pi^3}\iiint_{-\infty}^{\infty} d\xi\, d\eta\, d\zeta \cdot e^{-i\vec{F}_0\cdot\vec{r}} \cdot J^N$$



where $J = \frac{1}{V}\iiint e^{i\frac{r}{R^p}\cdot\omega_p} R^2 dR \cdot \sin\theta_1 d\theta_1 d\varphi_1 \cdot \sin\theta_2 d\theta_2 d\varphi_2$

$$V = \frac{4}{3}\pi R_{max}^3\, 4\pi = \frac{16\pi^2 R_{max}^3}{3}$$

$\vec{r} = \xi\vec{i} + \eta\vec{j} + \zeta\vec{k}$;

The values of J^N are

$p=2$: $J_2^N = e^{-\frac{8\sqrt{2\pi}}{15}\pi n r^{3/2} r^{3/2}} = e^{-4.21\, n r^{3/2} r^{3/2}} = e^{-C_2 r^{3/2}}$

n = number of ions per c. c. $\quad C_2 = 4.21\, n e^{3/2}$

$p=3$: $J_3^N = e^{-\frac{4\pi}{3}\mu r \cdot i n \overline{\omega_3}}$; $\overline{\omega_3} = \frac{1}{16\pi^2}\int \omega_3 \log\omega_3\, d\Omega_1 d\Omega_2$

$= -\pi i \times$ ~~0~~ 0.345 by graphical computation

$J_3^N = e^{-4.54 r\mu n} = e^{-C_3 r}$

$p=4$: $J_4^N = e^{\left\{e^{i\frac{5\pi}{8}} \cdot \Gamma\left(\frac{1}{4}\right) \cdot \frac{4\pi}{3} n \cdot \left(\frac{Ar}{2}\right)^{3/4} \cdot \overline{\omega_4}\right\}}$

where $\overline{\omega_4} = \frac{1}{16\pi^2}\int\cdots\int d\Omega_b\, d\Omega'\, \omega_4^{3/4} = 1.66\left(1 + i^{3/2}\right)$

by graphical computation.

$$J_4^N = e^{-11.49\, n\cdot (Ak)^{3/4}} = e^{-c_4 k^{3/4}}$$

where $c_4 = 11.49\, n A^{3/4}$.

For all three cases

$$J_p^N = e^{-c_p k^{3/p}} \quad \text{where } p = 2, 3, 4$$

$$c_2 = 4.21\, n e^{3/2} \; ; \; c_3 = 4.54\, n\mu \; ; \; c_4 = 11.49\, n A^{3/4}$$

$$W(F_0) = W(\vec{F_0}) \cdot 4\pi F_0^2$$

Define $F_n = c_2^{2/3}$ $= 2.61\, n^{2/3} e$ for ~~dipoles~~ coins

$F_n = c_3$ $= 4.54\, n\mu$ for dipoles

$F_n = c_4^{4/3}$ $= 25.67\, n^{4/3} A$ for quadrupoles.

Define $\beta = \dfrac{F_0}{F_n}$

For ~~dipoles~~ coins

$$W(\vec{F_0}) = \frac{1}{2\pi^2} \cdot \frac{2}{3} \cdot \frac{1}{F_0^3} \int_0^\infty e^{-\frac{c_2 v}{F_0^{3/2}}} \cdot v^{1/3} \cdot \sin v^{3/3} \cdot dv$$

$$v = (F_0 k)^{3/2}$$

For v small the sine function is expanded as a series of powers of v & for v large the exponential is expanded & the sine function is written in complex form. Term by term integration gives two series in Γ functions.

For β small, $W(F_0)\, dF_0 = d\beta \cdot \dfrac{4\beta^2}{3\pi}\left\{1 - 0.4628\,\beta^2 + 0.1227\,\beta^4 - 0.02325\,\beta^6 + \cdots\right\}$

For β large, $W(F_0)\, dF_0 = d\beta \cdot \dfrac{2.350}{\pi \beta^{5/2}}\left\{1 + \dfrac{5.106}{\beta^{3/2}} - \dfrac{7.4375}{\beta^{6/2}} + \dfrac{0.000}{\beta^{9/2}} - \cdots\right\}$

A graph has been drawn from a table of values given by Chandrasekhar. For the range $3.4 < \beta < 4.4$ both series ~~diverge~~ do converge too slowly.

The Holtzmark distribution is important in astronomy since the distribution of gravitational field due to a random distribution of stars is also given by the same formula. The difference is that in one case distance is about 100 A.U. and in the other case near 3 parsecs (10^{12} miles).

For dipoles the integration over ξ & ζ can be performed directly

$$W(F_0)\,dF_0 = d\beta \cdot \frac{4}{\pi}\frac{\beta^2}{(1+\beta^2)^2}.$$

For quadrupoles for ~~large~~ large β a series expansion ~~of~~ converging permits integration ~~in~~ term by term giving a series in β^n functions. For $0 < \beta < 1$ the integral has to be evaluated graphically.

For β small $W(F_0)\,dF_0 = \frac{4}{3}\cdot\frac{4}{\pi}\cdot\beta^2 d\beta\left\{1 - 2\cdot44\beta^2 + 11\cdot25\beta^4 - 72\beta^6 + \ldots\right\}$

For β large $W(F_0)\,dF_0 = \frac{4}{\pi}\cdot\frac{d\beta}{\beta^{9/4}}\cdot 0\cdot805\left\{1 - 0\cdot730\frac{1}{\beta^{3/4}} - 0\cdot328\frac{1}{\beta^{6/4}} + 0\cdot621\frac{1}{\beta^{9/4}} - 0\cdot163\frac{1}{\beta^{12/4}}\ldots\right\}$

Holtzmark calculates the line profile by means of the eqn

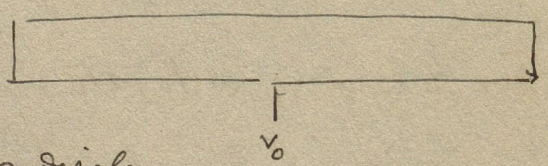
$$J(\nu)\,d\nu = d\nu \int_{F'}^{\infty} \frac{f}{2\nu_m} W(F)\,dF.$$

where F' is the field which produces a shift $(\nu - \nu_0)$ for the outermost component and f is a constant.

The weightage factor $\frac{f}{2\nu_m}$ is introduced on the assumption that for any given field the $2\nu_m$ distribution of J with ν can be replaced by a rectangular "block" of height h & base $2\nu_m = 2(\nu - \nu_0)$ where

$h \times 2\nu_m = f$ ~~the total~~

f being the intensity of the whole line.



The line profile was obtained by actual integration for a dipole field

$$J(\nu)\,d\nu = d\nu \cdot \frac{f}{2CF_n}\cdot\frac{4}{\pi}\cdot\frac{1}{(1+\beta'^2)} \quad \text{where } \beta' = \frac{2(\nu-\nu_0)}{CF_n}$$

& $2(\nu - \nu_0) = CF'$.

This expression has yields a half-intensity width

$$\Delta\nu_{1/2} = 4\cdot54\ C \text{ m.}\mu.$$

The profile for quadrupole is obtained by graphical method. It is very nearly the same as for dipoles.

The profile for ionic-field is obtained graphically. The profile falls to zero more rapidly on the wings.

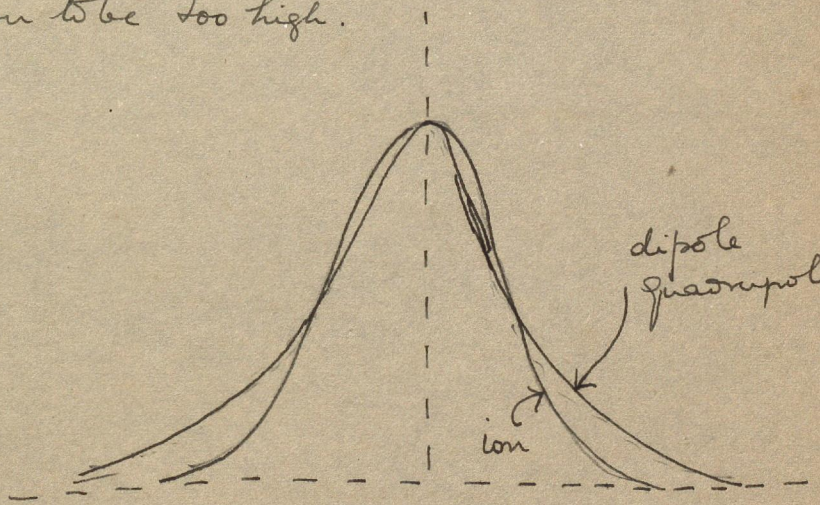
Half-intensity widths in the three cases are

ion $\quad \Delta\nu_{1/2} = 3.25\ C.\ n^{2/3}\ e.$

dipole $\quad \Delta\nu_{1/2} = 4.54\ C.\ n.\ \mu$

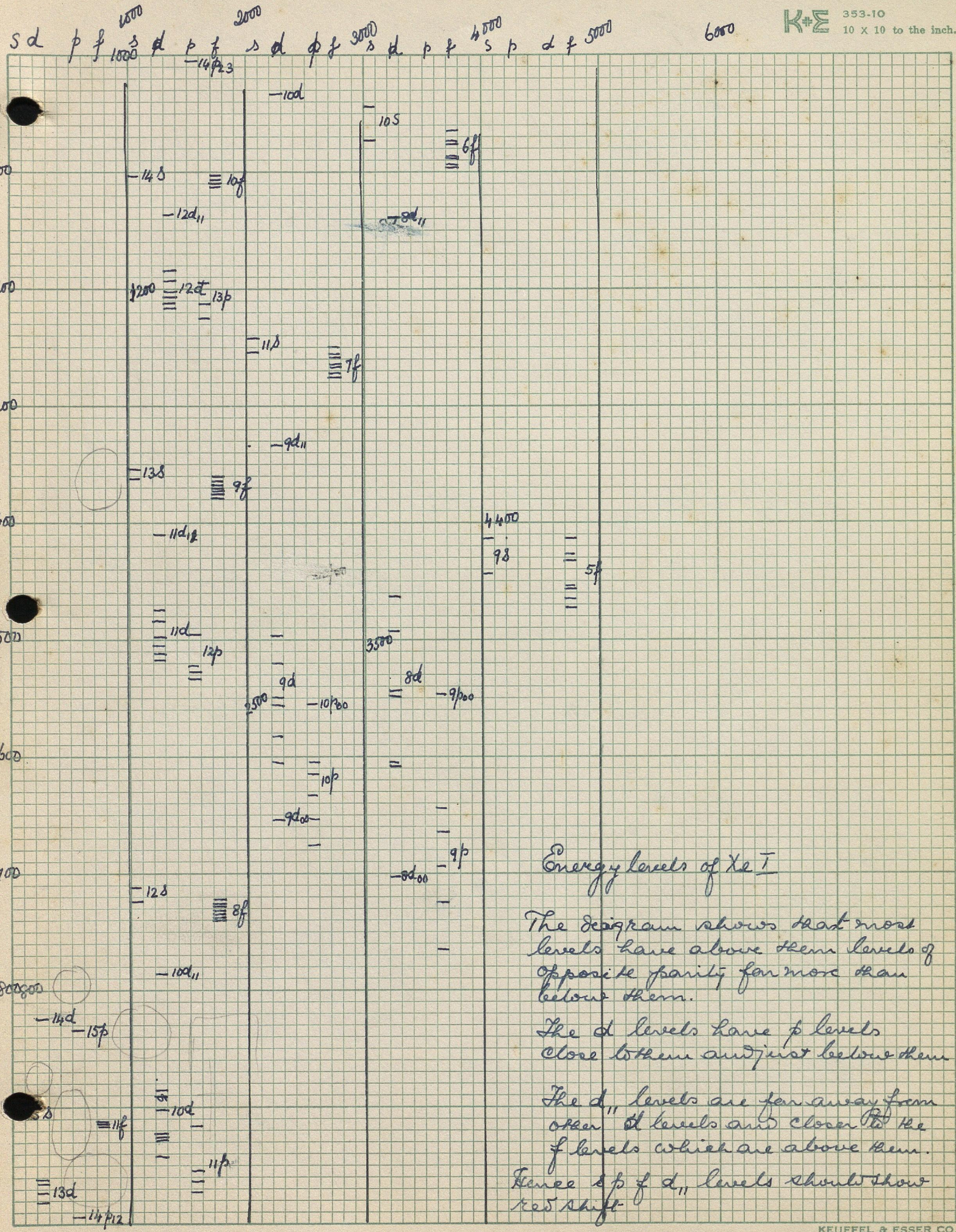
quadrupole $\quad \Delta\nu_{1/2} = 17.2\ C.\ n^{4/3}\ A.$

Holtsmark's explanation of the observations of Michaelson on the broadening of H_α line for pressures of H_2 between $\frac{1}{10}$ to 20 cm of Hg is often cited as an illustration of the theory. Holtsmark assumed that the broadening is due to the quadrupole moment of H_2. The observed values are considerably higher (by 70%) than calculated values & besides Holtsmark had assumed 3.2×10^{-26} as the value of A which is now known to be too high.



H_α line profile.

K+E 353-10
10 X 10 to the inch.



Energy levels of $_{54}Xe^{131}$

The diagram shows that most levels have above them levels of opposite parity far more than below them.

The d levels have p levels close to them and just below them

The d_{11} levels are far away from other d levels and closer to the f levels which are above them.

Hence s p f d_{11} levels should show no shift

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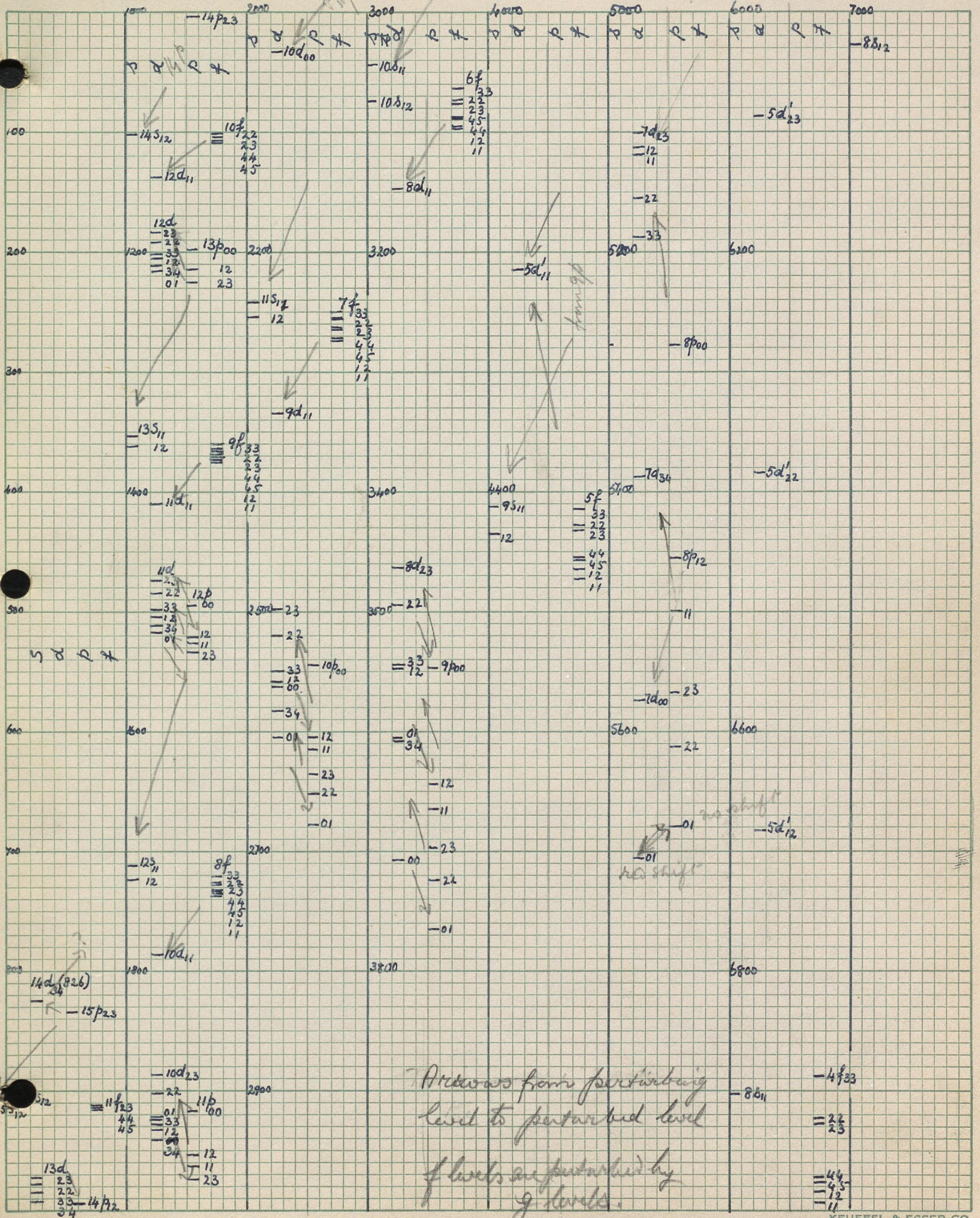
ENERGY LEVELS OF XENON I

K+E 353-10
10 X 10 to the inch.



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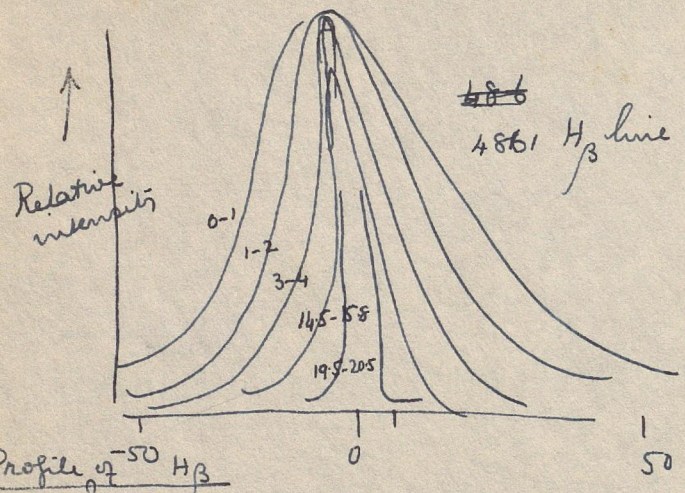
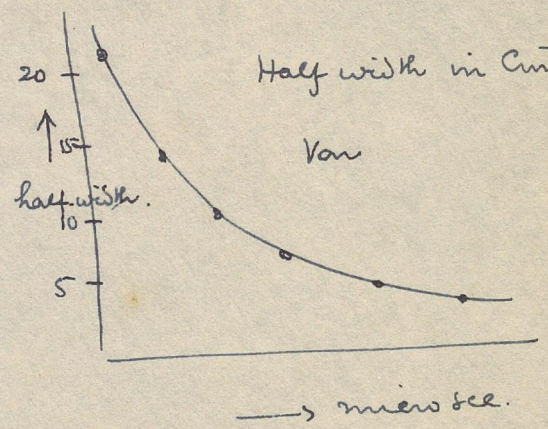
Broadening of Spectrum lines Vs Time

Extract from Dr. Stenhaus' Thesis.





Iron electrodes, 3 mm apart
Helium gas at atmospheric pressure

Both Craggs & Hopwood (17) & Fowler, Atkinson & Lee (18) have investigated the broadening of H_β experimentally & interpreted the results with the theory of Holtsmark. (19). They conclude that the broadening of H_β that they observe is due to the Stark effect produced & caused by the random electric fields about the atom created by the ions.

Craggs and Hopwood (17) tried to observe the change in profile of H_β Vs time in the spark discharge, but they were unable with their apparatus to observe it.

Comparing half-widths with Craggs & Hopwood the initial ion density is 1×10^{16} ions per c.c. decaying to 4.5×10^{14} ions per c.c.

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(17) Craggs & Hopwood: Proc Phys. Soc. (London) 59, 755 (1947.)

(18) Fowler, Atkinson and Lee - Summary Report. Project No NR071. University of Oklahoma (1951)

(19) Holtsmark Ann. Phys. Lpz 58 577, (1919)

Spitzer - P R. 55, 699, 1939.

The broadening of spectral lines due to very slow encounters can be calculated on a rigorous basis. This has been done by Holtzmark and Margenau for various potential laws.

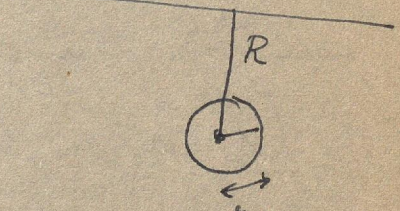
The "impact broadening" due to fast particles has been less thoroughly investigated. The Weisskopf assumption that (1) wave trains separated by a phase shift more than unity are incoherent and (2) ~~A mean~~ twice the mean time between such slow encounters is the effective damping constant is (a) formally incorrect for frequencies far removed from the line centre and (b) neglects the effect of the more distant encounters.

The method of smearing the statistical distribution over some kind of impact distribution is valid only if the proper smearing function is chosen. The dispersion curve sometimes chosen leads to quite erroneous results.

The following treatment applies to Hydrogen. We assume that linear Stark effect alone need be considered and that the Coulomb field due to an ion is homogeneous over the whole orbit of the electron.

$r_e \simeq \frac{3n^2a}{2}$ ~~a is~~ a = radius of 1st Bohr orbit

is when $R \sim 10\, r_e$ the Coulomb field deviates from the average value by 20%



Hence the theory is not valid for $R < 8\times10^{-8} n^2$.

For this distance $R > $ ~~8x10~~ $8n^2$ A. U. ~~the ratio of linear~~ $\frac{\Delta\nu_1}{\Delta\nu_2} > 1.50$, where $\Delta\nu_1$ = linear shift ; $\Delta\nu_2$ is quadratic Shift F

for $\Delta E_1 = -\frac{3}{2} n(k_1 - k_2) e F a$ (linear) ; $a = \frac{\hbar^2}{me^2}$

$\Delta E_2 = -\frac{a^3 F^2}{16} n^4 \left(17n^2 - 3(k_1-k_2)^2 - 9m^2 + 19\right)$; $F = \frac{e}{R^2}$.

We assume that each collision may be considered isolated from the others. This simplifies the analysis, but is not restrictive because the probability function

falls of ~~logarithmically~~ exponentially

A change in potential is adiabatic and will leave unchanged the quantum state of a system if the change occurs sufficiently slowly.

~~We consider a transition from a given Stark modified sub-level of A to a given~~ Given two levels A & B, we consider the given Stark effect component of the line $\nu_{AB} = \nu_0$.

$$\hbar \Delta_A = (E_A - E_{A0}) \quad (= \tfrac{R}{3^2}) \; ; \quad \hbar \Delta_B = (E_B - E_{B0}) \quad (= \tfrac{R}{2^2}) \; ; \quad x = 2\pi(\nu - \nu_0) \quad (H\alpha)$$

Δ_A, Δ_B, E_A, E_B, x, ν are evidently time-dependent.

$$J(x)\,dx = \frac{\gamma}{2\pi} \left| \int_0^{\infty} e^{i\left(x + \frac{i\gamma}{2}\right)T} \cdot dT \cdot e^{-i\int_0^T (\Delta_A - \Delta_B)\,d\tau} \right|^2 \cdot dx \quad (2)$$

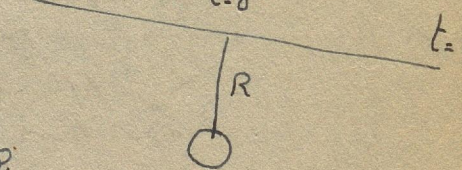
For the given component $\Delta_A = \frac{3\hbar}{2me} \cdot n(k_1 - k_2) \cdot F$.

k_1, k_2 are quantum numbers for the ξ, η components; $n = k_1 + k_2 + |m| + 1$.

$$F = \frac{Ze}{R^2} \; ; \quad R^2 = R^2 + v^2(T - t_0)^2 .$$

$$\Delta_A - \Delta_B = \frac{g}{\hbar} \cdot \frac{1}{R^2} \; ; \quad \frac{g}{\hbar} = \frac{3\hbar g Z}{2m} = 1.73\, g Z \; ; \quad g = \left[n(k_1 - k_2)\right]_A - \left[n(k_1 - k_2)\right]_B$$
$$= p\, n_A^2 \quad \text{where } |p| < 1$$

Total phase shift ~~for~~ due to the encounter is



$$\int_{-\infty}^{\infty} (\Delta_A - \Delta_B)\,d\tau = \int \frac{g}{\hbar R^2}\,d\tau = \frac{g}{\hbar R^2} \int \frac{d\tau}{1 + \left(\frac{v\tau}{R}\right)^2}$$

$$= \frac{g}{\hbar R v} \cdot \int \frac{d\left(\frac{v}{R}\tau\right)}{1 + \left(\frac{v}{R}\tau\right)^2} = \frac{g}{\hbar R v} \left[\tan^{-1} \frac{v\tau}{R} \right]_{-\infty}^{\infty} = \frac{\pi g}{\hbar R v} .$$

$$\delta = 2.19 \times 10^8 \frac{p\, n_e}{v R} \quad (= 1.73 \frac{p\, n_A^2}{v R})$$

We denote by δ the quantity $\frac{g}{\hbar R v}$; & we set $\xi = \frac{x R}{v}$; $u = \tau \frac{v}{R}$

$$x_n = \frac{g}{\hbar} \cdot \frac{1}{R^2}$$

(2) can be reduced to the form

$$J(x)\,dx = \frac{\gamma}{2\pi x^2} \left[1 + \frac{\Omega(\delta, \xi)}{\gamma} \delta^2 \left\{ \int_{-\infty}^{\infty} \frac{e^{i(\xi u - \delta \tan^{-1} u)}}{1 + u^2}\,du \right\}^2 \right] dx \quad (3)$$

$J(x)\,dx$ gives the line profile for the given k_1, k_2 component due to all ~~collisions~~ encounters at least distance R & velocity v.

$\Omega_\delta(\delta, \xi)$ is the number of such encounters p.s.

We denote $\int_{-\infty}^{\infty} \frac{e^{i(\xi u - \delta \tan^{-1} u)}}{1+u^2}\,du$ by $f_\delta(\xi)$ (3)

$f_\delta(\xi)$ is evidently a function of $\xi = \frac{xR}{v}$ and involves δ as a parameter.

$u = \frac{v}{R}\cdot\tau$ and hence $f_\delta(\xi)$ is an integral over the whole path of the ion.

Eqn (3) may be rewritten in the form

$$J(x)\,dx = \frac{\gamma}{2\pi}\,\frac{1}{x^2+\left(\frac{\gamma}{2}\right)^2}\cdot\left(1+\frac{\Omega\delta^2 f^2}{\gamma}\right)$$

$$= \frac{\gamma+\Omega\delta^2 f^2}{2\pi\left\{x^2+\left(\frac{\gamma}{2}\right)^2\right\}}$$

The ~~curves~~ expression for $f_\delta(\xi)$ can be evaluated for integral values of δ in terms of Bessel functions $K_\nu(\xi)$ of the second kind for imaginary argument.

$x_n = \frac{x\delta}{\xi} = \frac{\gamma}{\hbar}\cdot\frac{1}{R^2}$ = frequency shift due to ion placed at distance R from the atom.

The curves show how due to the encounter with the ion the profile of natural broadening is altered. If the ion moves very slowly ($\delta \to \infty$) the line moves upto a maximum $x_n^{\uparrow}$ & then goes back to ν_0. Due to a very rapid ion the line spreads out considerably more, and even to negative side of ν_0.

All $f_\delta^2(\xi)$ curves fall off as $\xi^\alpha e^{-2\xi}$.

Hence if ~~we~~ we try to get the line profile from the statistical case by the use of a smearing function, the function so employed must fall off at least as fast as $\xi^\alpha e^{-2\xi}$.

The dispersion curve ~~does~~ sometimes employed does not meet this ~~fast~~ requirement. The block or triangle function

used by Margenau is a better approximation.

For ~~$\xi = x$~~ $\xi = x\frac{R}{v}$ sufficiently small, i.e. if the value of $J(x)$ when summed over all collisions for which $\delta > \frac{1}{\pi}$ gives the result of Weisskopf.

Spitzer considers how the eqn for $J(x)$ is altered if the motion of the ~~atom~~ ion is so fast that the adiabatic approximation is not valid.

It is seen that in this case also the shape of the line profile is given by the adiabatic approximation provided ~~provided~~ δ is replaced by $\sigma = \sqrt{1+\delta^2}$. This result is proved strictly only for the two limiting cases of δ large & δ small.

Spitzer: P. R ~~Spitzer~~ 56, 39, 1939.

We have now to integrate $J(x)$ over all values of ξ & δ, i.e. over all values of R & v.

$$J(x) = \frac{\gamma}{2\pi x^2}\left\{1 + \frac{1}{\gamma}\cdot\sum_m \int_0^\infty dv \int_0^s \Omega_m'(Rv)\,\delta^2 f_\sigma^2(\xi)\,dR\right\} \qquad (4)$$

$\sum_m$ indicates summation over all types of ion.

The upper limit for R is set to be s where $\frac{4}{3}\pi s^3 N = 1$. N being the number of ions of type m.

For $R > s$, the encounters are screened by nearer ions, & besides the results depend only logarithmically on ~~R~~ R. this upper limit of R.

The formation of $J(x)$ for given δ, ξ is admittedly inaccurate for ~~δ~~ $R < 10$ A.U., but it is preferable to include an inaccurate value than to ignore the effect of close encounters.

Assuming Maxwellian distribution,

$$\Omega(Rv)\,dR\,dv = 2\pi R\,dR\cdot\frac{4}{\alpha^3\sqrt{\pi}}\,v^2 e^{-\frac{v^2}{\alpha^2}}\,dv$$

$\alpha = \sqrt{\frac{2RT}{\mu}}$ μ = reduced mass of atom & ion.

(4) ~~R~~ reduces to

$$J(x)\,dx = \frac{\gamma}{2\pi x^2}\left\{1 + \frac{4}{\gamma}\sqrt{\frac{\pi}{\alpha}}\gamma_1\cdot\left(\frac{q}{\hbar}\right)^{3/2}\cdot H(x)\right\}$$

or more simply $J(x) = \frac{\gamma}{2\pi x^2}\left\{1 + \frac{4\sqrt{\pi}\cdot x}{\gamma\alpha}\left(\frac{q}{\hbar}\right)^2 H(x)\right\}$

The summation over n has been dropped.

$$H = \int_0^\infty e^{-u} du \int_{\gamma_1/\gamma_2\sqrt{u}}^{\infty} \frac{f_\sigma^2(\xi)}{\xi} d\xi .$$

$\gamma_1 = \frac{q}{\hbar} \frac{x}{\alpha^2}$; $\gamma_2 = \frac{q}{\hbar . s . \alpha}$; $\gamma_3 = \left(\frac{2}{\alpha s} . x\right)^2$; $u = \frac{v^2}{\alpha^2}$; $\delta = \frac{q}{\hbar R v}$; $\xi = \frac{R}{v} x$; $\frac{\gamma_1}{\gamma_2\sqrt{u}} = \frac{\delta x}{v}$

γ_2 is $\frac{1}{\pi}$ times phase shift due to an ion with distance s & velocity α (the most probable ion)

$\therefore \gamma_1 = \beta \gamma_2^2$

$\frac{\gamma_1}{\gamma_2^2} = \frac{x}{x_n^*}$ and is practically equal to Holtzmark's ratio $\beta = \frac{F}{F_n}$.

Holtzmark's value of $F_n = \left\{\frac{8\pi\sqrt{2\pi}}{15}\right\}^{2/3} . Ze s^{-2/3}$

$= 1 \cdot 0018 \frac{Ze}{s^2}$

viz the Holtzmark value of normal field strength is the field due to a stationary ion at average distance s.

The evaluation of $H(x)$ is possible only by an approximate method.

We set $f_\sigma(\xi) = f_\sigma(0)$ for $\frac{x}{x_n^*} < \frac{1}{16}$

$\therefore f_\sigma(\xi) = f_1(\xi)$ $\quad 1 < \sigma < 1.5$

$= f_2(\xi)$ $\quad 1.5 < \sigma < 3$

$= f_4(\xi)$ $\quad 3 < \sigma < 5$

$= f_\infty(\xi)$ $\quad 5 < \sigma .$

Define $L(x,u) = \int_0^\infty \frac{f_\sigma^2(\xi)}{\xi} d\xi$

$H(x) = H^1(x) - H^2(x)$

where $H^1(x) = \int_0^\infty e^{-u} du . L(x,u)$; $H^2(u) = \int_0^\infty e^{-u} du \int_{\frac{\gamma_1}{\gamma_2\sqrt{u}}}^{\infty} \frac{f_\sigma^2(\xi)}{\xi} d\xi$

From ~~known~~ (3)

$$\frac{f_\sigma^2(0)}{\xi}\,d\xi = \frac{4\sin^2\frac{\pi\sigma}{2}}{\sigma(\sigma^2-1)}\cdot d\sigma$$

$$\frac{f_1^2(\xi)}{\xi}\,d\xi = 4\xi\left\{K_1^2(\xi)+K_0^2(\xi)\right\}d\xi$$

$$\frac{f_2^2(\xi)}{\xi}\,d\xi = 4\pi^2\xi\, e^{-2\xi}\cdot d\xi$$

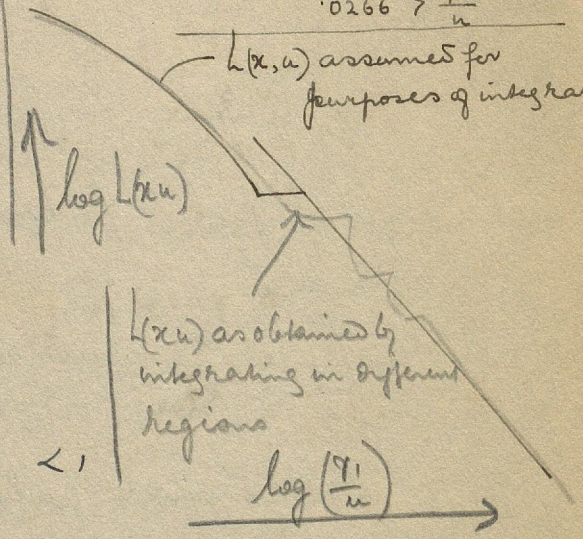
$$\frac{f_4^2(\xi)}{\xi}\,d\xi = 2\pi^2\xi(1-\xi)^2\cdot e^{-2\xi}\,d\xi.$$

$$\frac{f_\infty^2(\xi)}{\xi}\,d\xi \begin{cases} = \frac{\pi}{2}\left(\frac{u}{\gamma_1}\right)^{1/2}\cdot\frac{d\beta}{\sqrt{1-\beta}} & \text{for } \beta<1 \\ = 0 & \text{for } \beta>0 \end{cases}$$

$L(xu) = \pi\left(\frac{u}{\gamma_1}\right)^{1/2}$ for $\frac{\gamma_1}{u} > .0520$

$= 13.80$ for $.0520 > \frac{\gamma_1}{u} > .0266$

$= 4\log\left(\frac{u}{\gamma_1}\right) - 0.69$ for $.0266 > \frac{\gamma_1}{u}$



For $\gamma_1 > .10$, $H'(x) = \frac{\pi^{3/2}}{2\sqrt{\gamma_1}}$ } ± 5%.

$\gamma_1 < .03$ $\quad H'(x) = 4\log\left(\frac{1}{\gamma_1}\right) - 3.02 + 6.1\gamma_1$ }

In the intermediate region $H'(x)$ is ~~known~~ by ~~interpolation~~.

$H'(x) = \pi^{3/2}\,\mathrm{erf}\,(4.39\sqrt{\gamma_1})\cdot\frac{1}{2\sqrt{\gamma_1}} + 4\,Ei\,(37.4\gamma_1)$ where $\mathrm{erf}(x) = \frac{2}{\sqrt{\pi}}\int_0^x e^{-t^2}dt$ & $Ei(x) = \int_x^\infty \frac{e^{-t}}{t}\,dt$.

We define $\gamma_3 = \left(2\frac{\gamma_1}{\gamma_2}\right)^2$. The contribution to $H^2(x)$ from $u < .032$ or $v < .18x$ is negligible
So we set $f_0^2(\xi) = f_1^2(\xi)$ & for $f_1^2(\xi)$ we substitute an approximating function.

When $\gamma_3 < .04$ we have, to less than 5%

$$F(z) = \int_0^\infty \frac{1}{u}\cdot e^{\left(-zu-\frac{1}{\sqrt{u}}\right)}\cdot du$$

$$H^2(x) = 4\log\left(\frac{\gamma_2}{\gamma_1}\right) - .688 - 6.7\frac{\gamma_1}{\gamma_2}\cdot$$

$$F'(z) = -\int_0^\infty e^{\left(-zu-\frac{1}{\sqrt{u}}\right)}du$$

For all γ_3, $H^2(x) = 2\left\{F(1.447\gamma_3) - \pi\gamma_3 F'(\gamma_3)\right\}$ ~~where~~

and if $\gamma_1 < \frac{\gamma_2}{10}$ & $\gamma_2 < .2$, we have, to within 10%

$$H(x) = 4\log\left(\frac{1}{\gamma_2}\right) - 2.33 + 6.1\gamma_1 + 6.7\frac{\gamma_1}{\gamma_2}.$$

Thus $H(x)$ approaches asymptotically a value independent of γ_1.

This asymptotic result holds also for $\beta < \frac{1}{16}$.

These formulas give the profile of any given component.

To compare the results with that of Holtzmark

$$W(\beta)\,d\beta = 2\,J(x)\,dx. \tag{36}$$

$$\therefore \beta^2 W(\beta) = 2J(x)\cdot\frac{x^2\delta^2\hbar}{q} = \frac{3}{\pi^{3/2}}\cdot\sum_m \gamma_2 H_m(x)\cdot\frac{N_m}{N} \tag{36b}$$

or if one type of ion is present $\beta^2 W(\beta) = \frac{3}{\pi^{3/2}}\gamma_2 H(x)$

The factor 2 has been introduced before $J(x)$ since the expressions for $J(x)$ were derived for both components and the area under $J(x)dx$ has been normalized to unity whereas $W(\beta)d\beta$ for a single component is normalized to unity.

Weiskopff's expression for intensity is

$$J(x)\,dx = \frac{b/\pi}{x^2+b^2}\,dx \quad \text{where } b = 2\pi^{5/2}\frac{q^2}{\hbar^2\alpha}\hbar n$$

The half intensity width is $\Delta\nu_{1/2} = \frac{b}{\pi}$ $\hbar$ if $\nu-\nu_0 \gg \frac{b}{\pi}$, $J(x) = \frac{b}{\pi x^2}$

This expression follows as a special case, but integrating

$$J(x) = \frac{\gamma}{2\pi x^2}\left\{1+\frac{\Omega}{\gamma}\delta^2 f_\sigma^2(\xi)\right\} \text{ from } 0 \text{ to } R'$$

and set R' such that $\delta = \frac{q}{\hbar v R'} = \frac{1}{\pi}$, and then integrate over v.

From (36) $\beta^2 W(\beta) = 3\sqrt{\pi}\,\gamma_2$ (39)

for $\beta^2 W(\beta) = 2J(x)\frac{x^2\delta^2\hbar}{q} = 2\cdot\frac{1}{\pi x^2}\,2\pi^{5/2}\frac{q^2}{\hbar^2\alpha}N\cdot\frac{x^2\delta^2\hbar}{q}$

$\hbar$ $\frac{4}{3}\pi\delta^3 N = 1$ $\hbar$ $\gamma_2 = \frac{q}{\hbar\delta\alpha}$

For large β the Weiskoff expn (39) gives too high a value since at low vel. ions the $W(\beta)$ falls off more rapidly than the dispersion curve — Weiskopff ignores the effect of very large phase shifts

For small β, eqn 39 gives too ~~low~~ a value of γ is high since the correction for adiabatic ~~wave function~~ conditions has not been made; $\hbar$ eqn 39 gives too low a value if γ is low because the distant encounters are neglected.

Holtzmark analysis gives the correct value for β large since large β is due to slow fluctuations in field strength. For small β the statistical value is too low due to the neglect of impact broadening.

The profile of a given line is due to the profiles of all its components.

$$J(x) = \frac{1}{2\pi x^2}\left\{\sum_j g_j \cdot \varphi_j + 4\sqrt{\frac{\pi}{x}} \cdot \frac{1}{\beta^{3/2}} \cdot \sum_j \sum_m N_m \cdot g_{mj}^{3/2} \sqrt{g_1}\, H_{mj}(x)\right\} \quad (40)$$

$$\varphi_j = \frac{f_j}{\sum_j f_j} \quad \text{the normalized oscillator strengths.}$$

It is estimated that the total probable error due to the mathematical approximations is $\leq 9.7\%$.

If both γ_1 and γ_2 are very different from unity, eqn (40) should be adequate to within 2%.

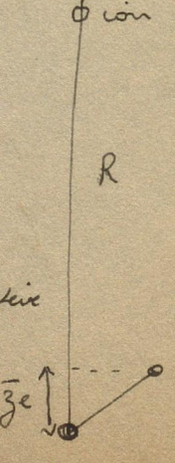
In an assembly containing equal number of positive ions & electrons, γ_2 for positive ions is usually greater than 1 and hence they produce the statistical effect. The contribution of the electrons which move much more rapidly is negligible.

The assumption of single encounters is adequate when γ_2 is less than $\frac{1}{5}$. Multiple encounters at close distances have negligible probability.

The error introduced by neglecting the inhomogeneity of the ionic field may be can be estimated by taking the average value of the perturbing potential.

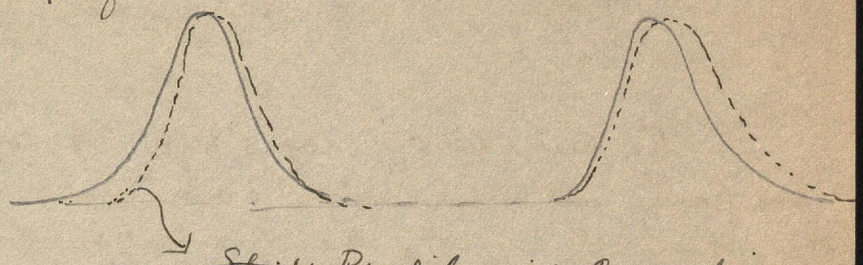
To a first approximation

$$\overline{V} = + \frac{Ze}{R^2}\overline{z_e} - \frac{Ze}{R^2}\overline{z_e}\left\{1 + \frac{\overline{z_e}}{R}\right\}$$



Thus in the more strongly shifted components the value we have assumed is smaller than the actual value in the ratio $1 + \frac{\overline{z_e}}{R}$ with an error $\approx$ or $\frac{\overline{z_e}}{R}$. The error is independent of the asymmetry of the sign of z_e and

produces an asymmetry of the line



~~Shift~~ Profile wise correction for inhomogeneity.

We recall

$$\Delta\nu_{AB} = \frac{g}{\pi R^2} = \frac{.275\, g\, Z}{R^2}$$

$$g = [n(k_2 - k_1)]_A - [n(k_2 - k_1)]_B = p\, n_A^2$$

where $|p|$ ranges from 0 to nearly 1.

The phase shift per encounter in units of π radians is

$$\delta = \frac{1.73\, p\, n_A^2}{v R} = 2.19 \times 10^8 \frac{p \cdot \bar{r}_e}{v R}$$

$\bar{r}_e$ is the average value of r_e in the upper state, & sublevel (i.e. $l = 0$)

The wavelength shift in A.U.

$$\Delta\lambda_{AB} = 1.22 \times 10^3 \left(\frac{\bar{r}_e}{R}\right)^2 \frac{p\, n_B^4}{n_A^2 \left\{1 - \left(\frac{n_B}{n_A}\right)^2\right\}^2}$$

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$$\gamma_1 = 2.18 \times 10^8\, p\, \frac{w}{T} \frac{\Delta\lambda}{\lambda} \left\{\left(\frac{n_A}{n_B}\right)^2 - 1\right\}$$

$$\gamma_2 = 2.18 \times 10^{-4}\, p \cdot \sqrt{\frac{w}{T}} \cdot n_A^2 \cdot N^{1/3}$$

T is the absolute temp; $w = \dfrac{m_{ion}}{m_{ion} + m_H}$

which for a proton is $\frac{1}{2}$, & for an electron is 5.4×10^{-4}

When R is $\geq 3\bar{r}_e$ the above theory breaks down. For the Balmer series, the distance $R = 3\bar{r}_e$ corresponds to a

$$\Delta\lambda_{AB} \approx \frac{2160}{n_A^2} \text{ A.U.} \quad \frac{2160}{49} = 40 \text{ AU for the } 5^{\text{th}} \text{ Balmer line}$$

Bat and is nearly 25 A.U. for the 7th Balmer line. But this is of the order of separation between successive Balmer lines.

The curves of $\log \beta^2 W(\beta)$ vs $\log \beta$ which for small β are horizontal and slope downwards illustrate what is called the Margenau effect, the transition from impact broadening to statistical broadening.

The profile is $J(x) = \frac{C}{x^2}$ for low values of $\beta = \frac{x}{x_0}$ or for low values of γ i.e. ~~is low for~~ small

As γ increases or as β increases for a given γ, the profile changes to

$$J(x) = \frac{C_1}{x^{5/2}}.$$

This is observed in the laboratory as a transition in the rate of line growth which takes place at with increasing pressure.

The values of $J(x)$ have a probable error of less than 10% except in the intractable region of γ_2 between .2 & 2 & at the same time γ_1 less than unity.

Craggs & Hopwood Proc. Phys. Soc. 59, 755, 1947.

Measurements were made on the H_α, H_β, H_γ lines in a spark channel. The spark was produced in a gap 5 mm wide. The pressure of H_2 was 85 mm of Hg. The half intensity widths of the lines were nearly 40 cm^{-1} for H_α; 100 cm^{-1} for H_β & 120 cm^{-1} for H_γ.

The broadening is assumed to be due solely to ions. Hence it is assumed that the Holtzmark distribution functions

$$W(F_0)\,dF_0 = \frac{4}{3\pi}\beta^2 d\beta\left\{1 + \cdot 4/\beta^2 \ldots\right\} \text{ for } \beta \text{ small}$$

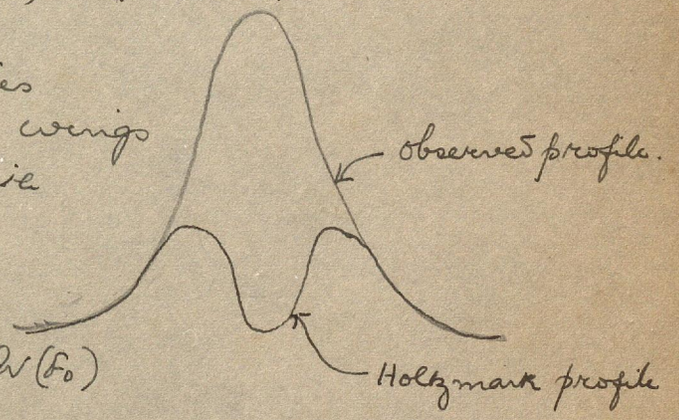
$$W(F_0)\,dF_0 = d\beta \cdot \frac{1}{\pi\beta^{5/4}} \times 2{\cdot}3\left\{1 + \frac{5}{\beta^{3/2}} - \frac{7}{\beta^{3}/_{2}} \ldots\right\} \text{ for } \beta \text{ large}$$

give the probability of the field having a value F.

It is also assumed that the intensity distribution $J(\alpha)$ is given by $W(F_0)\,dF_0 = J(x)\,dx$ for any one component.

$$\beta = \frac{F}{F_n} \quad ; \quad F_n = C_1 e N^{2/3} \quad ; \quad C_1 = 2{\cdot}61.$$

The value of F_n which gives the closest fit for the wings of the calculated profile with the observed profile is experimentally determined. The "calculated" profile is the weighted sum of the profiles $W(F_0)$ for each of the components



The value of N is found to be $(2{\cdot}5 \pm {\cdot}4) \times 10^{17}$ ions per c.c.

The corresponding value of γ_2 is

$$\gamma_2 = 2{\cdot}18 \times 10^{-4}\, p \sqrt{\frac{w}{T}} \cdot n_A^2\, N^{1/3}$$

$$= 2{\cdot}18 \times 10^{-4} \times \sqrt{\frac{1}{6400}} \times 9 \times (250)^{1/3} \times 10^5$$

$$= {\cdot}15\,p \quad \text{where } |p| \text{ ranges from 0 to nearly 1.}$$

Set $T = 3200$, n_A^2 for $H_\alpha = 9$, w for protons is $\frac{1}{2}$

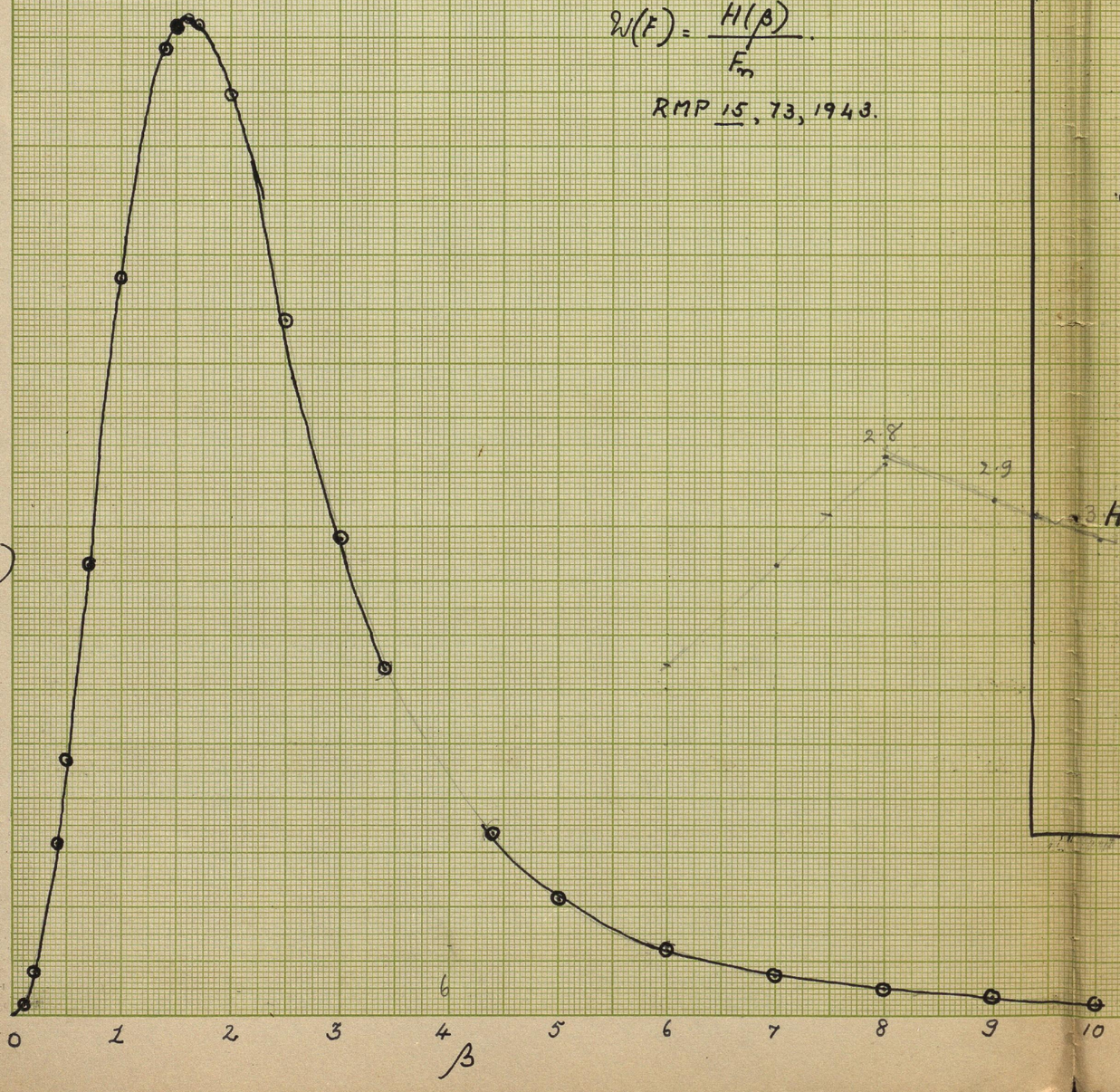
Hence the Statistical (Holtzmark) distribution is not valid except for the outermost components of H_β or H_γ.

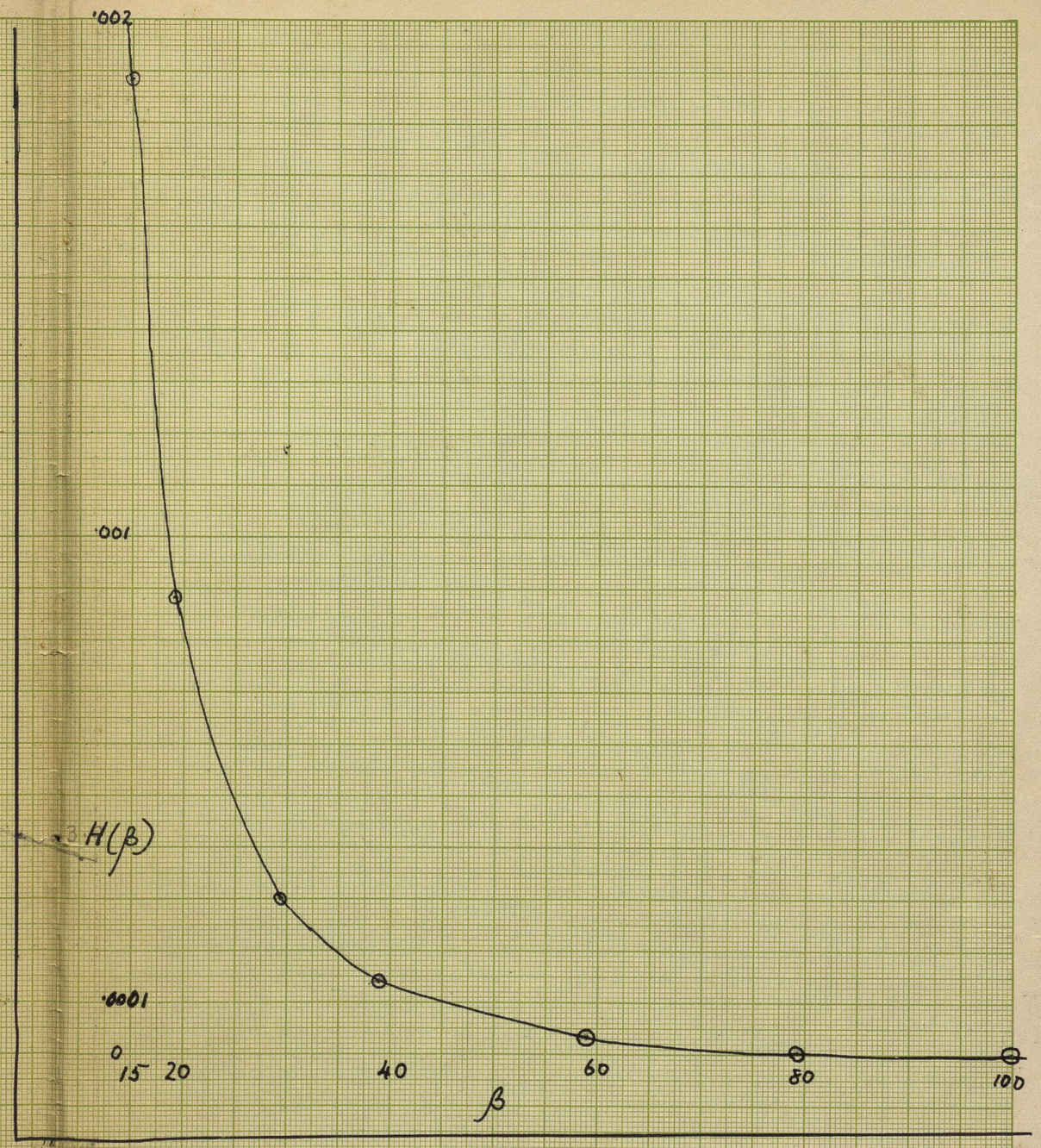
$H(\beta)$ vs β.

$$H(\beta) = \frac{2}{\pi\beta}\int_0^\infty e^{-\left(\frac{x}{\beta}\right)^{3/2}} x \sin x \, dx.$$

$$W(F) = \frac{H(\beta)}{F_m}.$$

RMP 15, 73, 1943.





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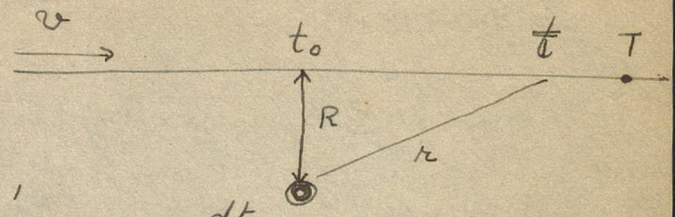
Spitzer PR. 55, 701, 1939



Proof of eqn 14

$$\int_{t_0}^{T}(\Delta_A - \Delta_B)\,dt$$

$$= \frac{2}{\hbar}\int_{t_0}^{T}\frac{1}{R^2 + v^2(t-t_0)^2}\,dt = \frac{2}{\hbar R^2}\int_{t_0}^{T}\frac{1}{1+\left[\frac{v}{R}(t-t_0)\right]^2}\,dt$$

Set $y = \frac{v}{R}(t-t_0)$ $\therefore dy = \frac{v}{R}dt$

$$= \frac{2}{\hbar R^2}\cdot\frac{R}{v}\int_{t_0}^{T}\frac{dy}{1+y^2} = \frac{2}{\hbar R v}\left[\tan^{-1}\frac{v}{R}(t-t_0)\right]_{t_0}^{T}$$

$$= \frac{2}{\hbar R v}\tan^{-1}\frac{v}{R}(T-t_0)$$ which is eqn 14.

$$\therefore \int_{-\infty}^{\infty}(\Delta_A - \Delta_B)\,dt = \frac{2}{\hbar R v}\cdot\pi = \pi\delta.$$

Proof of eqn 16

$$J(x) = \frac{\gamma}{2\pi}\left|\int_0^\infty e^{i\left(x+\frac{i\gamma}{2}\right)T}\cdot dT\cdot e^{-i\int_0^T(\Delta_A-\Delta_B)\,dt}\right|^2$$

$$= \frac{\gamma}{2\pi}\left|\int_0^\infty e^{i\left(x+\frac{i\gamma}{2}\right)T}\cdot dT\cdot e^{-i\frac{\pi\delta}{2}-i\int_{t_0}^{T}(\Delta_A-\Delta_B)\,dt}\right|^2$$

$$= \frac{\gamma}{2\pi}\left|\int_0^\infty e^{i\left(x+\frac{i\gamma}{2}\right)T}\cdot dT\, e^{-i\frac{\pi\delta}{2}-i\delta\tan^{-1}\frac{v(T-t_0)}{R}}\right|^2$$

$$= \frac{\gamma}{2\pi}\left|e^{-i\frac{\pi\delta}{2}}\cdot\frac{1}{i\left(x+\frac{i\gamma}{2}\right)}\left\{\left[e^{i\left(x+\frac{i\gamma}{2}\right)T-i\delta\tan^{-1}\frac{v(T-t_0)}{R}}\right]_0^\infty - \int_0^\infty e^{i\left(x+\frac{i\gamma}{2}\right)T}\cdot\frac{d}{dT}\left(e^{-i\delta\tan^{-1}\frac{v(T-t_0)}{R}}\right)dT\right\}\right|^2$$

$$= \frac{\gamma}{2\pi}\frac{1}{x^2+\left(\frac{\gamma}{2}\right)^2}\left|e^{-i\frac{\pi\delta}{2}}\left[e^{i\left(x+\frac{i\gamma}{2}\right)T-i\delta\tan^{-1}\frac{v(T-t_0)}{R}}\right]_0^\infty - e^{-i\frac{\pi\delta}{2}}\int_0^\infty\frac{e^{i\left(x+\frac{i\gamma}{2}\right)T}\cdot\left(-i\delta\frac{v}{R}\right)e^{-i\delta\tan^{-1}\frac{v(T-t_0)}{R}}}{1+\left(\frac{v(T-t_0)}{R}\right)^2}dT\right|^2$$

$$= \frac{\gamma}{2\pi}\frac{1}{x^2+\left(\frac{\gamma}{2}\right)^2}\left|-e^{-i\frac{\pi\delta}{2}}\cdot e^{i\frac{\pi\delta}{2}} + i\delta\frac{v}{R}e^{-i\frac{\pi\delta}{2}}\int_0^\infty\frac{e^{i\left(x+\frac{i\gamma}{2}\right)T}\cdot e^{-i\delta\tan^{-1}\frac{v(T-t_0)}{R}}}{1+\left[\frac{v(T-t_0)}{R}\right]^2}dT\right|^2$$

$$= \frac{\gamma}{2\pi}\frac{1}{x^2+\left(\frac{\gamma}{2}\right)^2}\left|i - \frac{\delta v}{R}e^{-i\frac{\pi\delta}{2}}\int_0^\infty\frac{e^{i\left(x+\frac{i\gamma}{2}\right)T-i\delta\tan^{-1}\frac{v(T-t_0)}{R}}}{1+\left[\frac{v(T-t_0)}{R}\right]^2}dT\right|^2$$

Spitzer PR 56, 44, 1939.

To prove eqn 38 from the Weisskopf theory.

The Lorentz line shape is $\dfrac{\text{Const}}{(\nu-\nu_0)^2+\left(\frac{1}{2\pi\tau}\right)^2}$

And since $\int_{-\infty}^{\infty} J(\nu)\,d\nu = 1$ (normalization condition)

$$J(\nu)\,d\nu = \left(\frac{1}{2\pi^2\tau}\right)\cdot\frac{1}{(\nu-\nu_0)^2+\left(\frac{1}{2\pi\tau}\right)^2}\cdot d\nu$$

The value of $\left(\frac{1}{\tau}\right)$ is the number of times p.s. the wave train becomes incoherent due to collision.

According to Lorentz theory, $\frac{1}{\tau}$ = number of collisions p.s.

i.e. $\frac{1}{\tau} = \pi\rho^2 n\bar{v}$

where ρ is the optical collision diameter

$\bar{v}$ is the average speed.

According to Weisskopf's theory,

$\frac{1}{\tau}$ is the number of times the ion gets sufficiently close so as to produce a phase shift equal or greater than unity.

Now, an ion moving with speed v at distance R produces phase shift $\frac{\pi\varrho}{\hbar R v}$ for a given component

It produces i.e. phase shift $\frac{2\pi\varrho}{\hbar R v}$ between the two components. If $\frac{2\pi\varrho}{\hbar R v} \gtrless \pi$, the wave train ceases to be coherent and requires a separate Fourier analysis from the succeeding wave train.

Hence the collision diameter $\rho = \frac{2\varrho}{\hbar v}$; & every ion of the most probable speed $\bar{v}$ causes a phase difference equal or $\gtrless \pi$ if its distance of closest approach is $\frac{2\varrho}{\hbar}\frac{\pi}{\bar{v}}$.

$$\therefore \frac{1}{\tau} = \pi\rho^2 n\bar{v} = \pi\cdot\left(\frac{2\varrho}{\hbar\bar{v}}\right)^2\cdot n\bar{v} = 4\pi^3\left(\frac{\varrho}{\hbar}\right)^2\cdot\frac{n}{\bar{v}} \quad \text{since } \bar{v} = \frac{2\alpha}{\sqrt{\pi}}$$

$$\frac{1}{\tau} = 2\pi^{3/2}\cdot\left(\frac{\varrho}{\hbar}\right)^2\cdot\frac{n}{\alpha} \quad \therefore \frac{1}{2\pi^2\tau} = \frac{2\pi^2}{\sqrt{\pi}}\left(\frac{\varrho}{\hbar}\right)^2\cdot\frac{n}{\alpha} \quad \text{or} \quad \frac{1}{2\pi\tau} = \pi^2 2\sqrt{\pi}\left(\frac{\varrho}{\hbar}\right)^2\frac{n}{\alpha}.$$

But $J(\nu)\,d\nu = \left(\frac{1}{2\pi^2\tau}\right)\frac{1}{(\nu-\nu_0)^2+\left(\frac{1}{2\pi\tau}\right)^2}\,d\nu$ But $(\nu-\nu_0) = \frac{x}{2\pi}$ $\therefore d\nu = \frac{dx}{2\pi}$

$$J(x)\,dx = \left(\frac{1}{2\pi^2\tau}\right)\cdot\frac{1}{\left(\frac{x}{2\pi}\right)^2+\left(\frac{1}{2\pi\tau}\right)^2}\cdot\frac{dx}{2\pi} = \frac{1}{\pi\tau}\cdot\frac{1}{x^2+\left(\frac{1}{2\pi\tau}\right)^2}\left(\frac{1}{\pi\tau}\right)\cdot\frac{1}{x^2+\left(\frac{1}{\tau}\right)^2}\,dx.$$

$$= 2\pi^{5/2}\cdot\frac{\varrho}{\hbar}\frac{n}{\alpha}\left\{\frac{1}{x^2+2\pi^{7/2}\left(\frac{\varrho}{\hbar}\right)^2\frac{n}{\alpha}}\right\}dx.$$

If $\frac{\pi\rho}{\hbar k\alpha} > 1$ i.e. if $R < \frac{\pi\rho}{\hbar\alpha}$, the wavetrain becomes incoherent.

∴ ρ in Weisskopf's theory is not the diameter of the molecule as in Lorentz theory but a larger quantity viz $\frac{\pi\rho}{\hbar\alpha}$ which is just sufficient to produce phase shift unity.

$$\frac{1}{\tau} = \pi\rho^2 n\bar{v} = \pi\cdot\left(\frac{\pi\rho}{\hbar\alpha}\right)^2 n\bar{v} \quad \text{since } \bar{v} = \frac{2\alpha}{\sqrt{\pi}}$$

$$\frac{1}{\tau} = 2\pi^{5/2}\cdot\left(\frac{\rho}{\hbar}\right)^2\cdot\frac{n}{\alpha}$$

$$J(\nu)\,d\nu = \frac{1}{2\pi^2\tau}\,\frac{1}{(\nu-\nu_0)^2+\left(\frac{1}{2\pi\tau}\right)^2}\,d\nu$$

Set $x = 2\pi(\nu-\nu_0)$ ∴ $d\nu = \frac{1}{2\pi}dx$

$$J(x)\,dx = \frac{1}{\pi\tau}\,\frac{1}{x^2+\left(\frac{1}{\tau}\right)^2}\,dx$$

$$= 2\pi^{3/2}\cdot\left(\frac{\rho}{\hbar}\right)^2\frac{n}{\alpha}\cdot\left\{\frac{1}{x^2+\left[2\pi^{5/2}\left(\frac{\rho}{\hbar}\right)^2\cdot\frac{n}{\alpha}\right]^2}\right\}dx.$$

when $x \gg 2\pi^{5/2}\left(\frac{\rho}{\hbar}\right)^2\frac{n}{\alpha}$

$$J(x)\,dx = \frac{2\pi^{3/2}\left(\frac{\rho}{\hbar}\right)^2\frac{n}{\alpha}}{x^2}\,dx.$$

This is the same as eqn (38)

$$J(x)\,dx = \frac{2}{\sqrt{\pi}}\sum_m \frac{\pi^2\cdot\rho^2 l_m^{1/2}\cdot n_m}{\hbar^2\cdot x^2} \quad \text{Since } l_m^{1/2} = \frac{1}{\alpha}.$$

Proof of eqn (8)

$R = \frac{\rho}{\hbar}$ We have to eliminate R, v, α & δ in terms of

$$\frac{\rho}{\hbar}, x, \gamma_1, u \text{ & } \xi.$$

We know

$$R = \left(\frac{\rho}{\hbar}\frac{xu}{\gamma'}\right)^{1/2}\cdot\frac{\xi}{x}\;;\quad v = \left(\frac{\rho}{\hbar}\cdot\frac{xu}{\gamma'}\right)^{1/2};\quad \alpha = \left(\frac{\rho}{\hbar}\frac{x}{\gamma'}\right)^{1/2};\quad \delta = \frac{\gamma_1}{\xi u}.$$

$$f(x) = \frac{\gamma}{2\pi x^2}\left\{1 + \frac{1}{\gamma}\cdot\int_0^{\infty}\int_0^{\delta} 2\pi R v\cdot N\cdot\frac{4}{\pi\alpha^3}\cdot e^{-v^2/\alpha^2}\cdot v^2\cdot\delta^2 f_\sigma^2(\xi)\,dR\cdot dv\right\}$$

$\frac{\gamma_1}{\gamma_2\sqrt{u}} = \frac{x\delta}{v}$ ∴ when $R = \delta$, $\xi = \frac{xR}{r} = \frac{x\delta}{r} = \frac{\gamma_1}{\gamma_2\sqrt{u}}$.

Other limits remain unchanged.

$$f(x) = \frac{\gamma}{2\pi x^2}\left\{1 + \frac{1}{\gamma}\cdot\int_0^{\infty}\int_0^{\frac{\gamma_1}{\gamma_2\sqrt{u}}} \frac{2\pi\left(\frac{\gamma}{\hbar}\frac{x\alpha}{\gamma_1}\right)^{1/2}\frac{\delta}{x}\cdot\left(\frac{\gamma}{\hbar}\cdot\frac{x\alpha}{\gamma_1}\right)^{1/2} 4N\cdot\frac{\gamma}{\hbar}\cdot\frac{x\alpha}{\gamma_1}\cdot e^{-u}\cdot\left(\frac{\gamma_1^{1/2}}{\xi^2\alpha^2}\right)\cdot f^2\left(\frac{\gamma}{\hbar}\frac{x}{x\gamma_1}\right)^{1/2}\cdot d\xi\cdot\frac{1}{2}\left(\frac{\gamma}{\hbar}\frac{x}{\gamma_1}\right)^{1/2}\frac{1}{\sqrt{u}}\,du}{\sqrt{\pi}\cdot\left(\frac{\gamma}{\hbar}\frac{x\alpha}{\gamma_1}\right)^{3/2}}\right\}$$

$$= \frac{\gamma}{2\pi x^2}\left\{1 + \frac{4}{\gamma}\left(\frac{\pi}{\alpha}\right)^{1/2}\cdot N\cdot\left(\frac{\gamma}{\hbar}\right)^{3/2}\cdot\gamma_1^{1/2}\cdot\int_0^{\infty} e^{-u}\,du\cdot\int_0^{\frac{\gamma_1}{\gamma_2\sqrt{u}}}\frac{f_\sigma^2(\xi)}{\xi}\,d\xi\right\}$$

To prove eqn 36 b which for one type of coins is $\beta^2 W(\beta) = \frac{3}{\pi^{3/2}}\gamma_2 H(x)$

$W(\beta)\,d\beta = 2f(x)\,dx$ ∴ $W(\beta) = 2f(x)\cdot\frac{dx}{d\beta}$ But $\frac{x}{x_{max}} = \beta$ ∴ $\frac{dx}{d\beta} = x_{max}$

$W(\beta) = 2f(x)\cdot x_{max}$ ∴ $\beta^2 W(\beta) = \frac{2f(x)\cdot x^2}{x_{max}}$

But $f(x) = \frac{\gamma}{2\pi x^2}\left\{1 + \frac{1}{\gamma}\cdot 4\sqrt{\pi}N\left(\frac{\gamma}{\hbar}\right)^2\cdot\frac{1}{\alpha}\cdot H(x)\right\}$

$\gamma_1 = \frac{\gamma}{\hbar\alpha^2}x$

$\left(\frac{\gamma_1}{x}\right)^{1/2} = \left(\frac{\gamma}{\hbar}\right)^{1/2}\frac{1}{\alpha}$

$$\beta^2 W(\beta) = \frac{4}{\sqrt{\pi}}\frac{N}{\alpha}\left(\frac{\gamma}{\hbar}\right)^2\cdot\frac{1}{x_{max}}\cdot H(x)$$

$$= \frac{4}{\sqrt{\pi}}\frac{N}{\alpha}\frac{x_{max}^2\delta^4}{x_{max}}\cdot H(x)$$

$$= \frac{4}{\sqrt{\pi}}\frac{N}{\alpha}\frac{\gamma_2\alpha}{\delta}\cdot\delta^4 H(x)$$

$$\beta^2 W(\beta) = \frac{3}{\pi^{3/2}}\cdot\gamma_2 H(x).$$

But $x_{max} = \frac{\gamma}{\hbar\delta^2}$ $\frac{\gamma}{\hbar} = x_{max}\delta^2$

$\gamma_2 = \frac{\gamma}{\hbar}\delta\alpha$ ∴ $x_{max} = \frac{\gamma_2\alpha}{\delta}$

$x_{max} = \frac{\gamma_2\alpha}{\delta}$

But $\frac{4}{3}\pi N\delta^3 = 1$

To show that Dirichlet's discontinuous integral

$$\frac{1}{\pi}\int_{-\infty}^{\infty} d\rho \frac{\sin\rho\frac{\Delta\nu}{2}}{\rho} e^{i(-\nu+\alpha\sum\frac{1}{n_i^6})\rho} = 1 \qquad \nu-\frac{\Delta\nu}{2} < -\sum\frac{\alpha}{n_i^6} < \nu+\frac{\Delta\nu}{2}$$

$$= 0 \qquad \text{for } \sum\frac{\alpha}{n_i^6} > \nu+\frac{\Delta\nu}{2} \text{ or } \sum\frac{\alpha}{n_i^6} < \nu-\frac{\Delta\nu}{2}$$

We evaluate the integral between finite limits $l/2$ to $-l/2$.

Set $\frac{\Delta\nu}{2} = a$; $\left(-\nu+\sum\frac{\alpha}{n_i^6}\right) = b$.

Since $\sin a\rho = \frac{e^{ia\rho}-e^{-ia\rho}}{2i}$

$$I = \frac{1}{\pi}\int_{-l/2}^{l/2} d\rho \frac{\sin\rho\frac{\Delta\nu}{2}}{\rho} e^{i(-\nu+\alpha\sum\frac{1}{n_i^6})\rho} = \frac{1}{2\pi i}\int\frac{d\rho}{\rho}\left\{e^{i(b+a)\rho} - e^{i(b-a)\rho}\right\}$$

Set $i(b+a) = \alpha$
$i(b-a) = \beta$

$$= \frac{1}{2\pi i}\left\{\int\frac{d\rho}{\rho}e^{\alpha\rho} - \int\frac{d\rho}{\rho}e^{\beta\rho}\right\}$$

Now $\int\frac{e^{\alpha\rho}}{\rho}d\rho = \log\rho + \alpha\rho + \frac{\alpha^2\rho^2}{2\cdot 2!} + \frac{\alpha^3\rho^3}{3\cdot 3!} + \cdots$

$$\therefore I = \frac{1}{2\pi i}\left\{\log\rho + \alpha\rho + \frac{\alpha^2\rho^2}{2\cdot 2!} + \cdots - \log\rho - \beta\rho - \frac{\beta^2\rho^2}{2\cdot 2!} - \frac{\beta^3\rho^3}{3\cdot 3!} - \cdots\right\}$$

$$= \frac{1}{2\pi i}\left\{(\alpha-\beta)\rho + \frac{\alpha^2-\beta^2}{2}\cdot\frac{\rho^2}{2!} + \frac{(\alpha^3-\beta^3)}{3}\cdot\frac{\rho^3}{3!} + \cdots\right\}$$

Now $\alpha-\beta = 2ia$; $\alpha^2-\beta^2 = i^2 2\cdot 2ab$; $\alpha^3-\beta^3 = 2i^3\cdot 3ab^2$

$\alpha^4-\beta^4 = 2i^4\cdot 4ab^3 \ldots$

neglecting terms in higher powers of $a = \frac{\Delta\nu}{2}$

$$\therefore I = \frac{1}{\pi i}\left\{iap + i^2ab\frac{\rho^2}{2!} + i^3ab^2\frac{\rho^3}{3!} + i^4ab^3\frac{\rho^4}{4!} + \cdots\right\}$$

$$= \frac{a}{\pi b}\left(b\rho - \frac{b^3\rho^3}{3!} + \frac{b^5\rho^5}{5!} - \cdots\right) + \frac{a}{\pi ib}\left(1 - \frac{b^2\rho^2}{2!} + \frac{b^4\rho^4}{4!}\right) - \frac{a}{\pi ib}$$

$$= \frac{a}{\pi ib}\cdot(\cos b\rho + i\sin b\rho)\Big|_{-l/2}^{l/2} = \frac{a}{\pi ib}e^{ib\rho}\Big|_{-l/2}^{l/2}$$

$$= \frac{a\,2i}{\pi ib}\,\frac{e^{ib\frac{l}{2}} - e^{-ib\frac{l}{2}}}{2i} = \frac{2a}{\pi b}\sin b\frac{l}{2} = \frac{\Delta\nu\cdot l}{2\pi}\cdot\frac{\sin b\frac{l}{2}}{b\frac{l}{2}}$$

~~Now for a given variable b, as $\frac{l}{2}$ tends to ∞, $\frac{\sin b\frac{l}{2}}{b\frac{l}{2}} = 1$ for~~

Let l be very large and finite. As b increases from zero up

$\frac{\sin b\frac{l}{2}}{b\frac{l}{2}}$ is 1 for $b=0$; decreases to zero for $b\frac{l}{2}=\frac{\pi}{2}$ or $b=\frac{\pi}{l}$ and oscillates between very small values for $b>\frac{\pi}{l}$

Let $\Delta\nu \to 0$ as $l \to \infty$ so that $\frac{\Delta\nu \cdot l}{2\pi}$ remains equal to unity.

Thus at $b=0$, $\frac{\Delta\nu \cdot l}{2\pi} \cdot \frac{\sin b\frac{l}{2}}{b\frac{l}{2}} = 1$.

at $b \gtrsim \frac{\pi}{l}$, $l \gtrsim \frac{\pi}{b}$ But $l = \frac{2\pi}{\Delta\nu}$

$\therefore$ at $b \gtrsim \frac{\pi}{l}$, $\frac{2\pi}{\Delta\nu} \gtrsim \frac{\pi}{b}$ or $b \gtrsim \frac{\Delta\nu}{2}$

And since when $b \gtrsim \frac{\pi}{l}$, the function $\frac{\sin b\frac{l}{2}}{b\frac{l}{2}} = 0$ for l very large,

for $\left|\alpha\sum\frac{1}{\lambda_i^b} - \nu\right| \gtrsim \frac{\Delta\nu}{2}$, $\frac{\sin b\frac{l}{2}}{b\frac{l}{2}} = 0$.

In other words the integral is unity for $\alpha\sum\frac{1}{\lambda_i^b}$ in the region $\left(\nu - \frac{\Delta\nu}{2}, \nu + \frac{\Delta\nu}{2}\right)$ and zero outside.