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Studies of alkali metals

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STUDIES OF ALKALI METALS

being a comparison of their activities, vapor
pressures and distributions in a closed system
at ordinary temperatures, with special reference
to their use in the rare gas content UX-874
voltage regulator tube.

A dissertation presented to the Depart-
ment of Chemistry of Union College in partial
fulfillment of the requirements for the degree
of Master of Science in Chemistry by

Name *Lester Clark Lewis*

Approved by *Charles B Hurd*

May 21, 1927.

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INTRODUCTION

Studies of the alkali metals have a directness
that leads to progress in both our general knowledge
of chemistry and in common usefulness, which so en-
courages and rewards the advance of pure knowledge.

As commonly studied, in combination, they react
so simply that we study them when we look for simplicity.
They seldom exhibit confusing multiple valence; their ions
(save for Li^+) are very mobile in solution; reactions
involving them move with considerable and well-observable
speed. Yet their very activity prevents us from studying
them as metals in air. To be sure, we may maintain for
a while amalgams of lithium, sodium and potassium. But,
for the writer at least, there lies lively interest in
observing the behavior of the pure metals over long
periods at ordinary temperatures.   And this privilege
has come through the uses developed in evacuated devices,
with the accompanying facilities for preparation and observa-
tion developed for these uses.

At the present time there are two uses: the first
concerns electronic emission from a much hotter body in the
presence of alkali metal vapor at room temperature - the
second is the rendering operable at ordinary voltages
electrical devices using low pressures of gas (principally rare

gases to avoid reaction and gradual change of character-
istics). This thesis will deal with the second use, the
successful application of which has engaged the writer
for the past year.

HISTORICAL

For at least fifty years, during which gaseous dis-
charges have been studied, it has been known that the
alkali metals produced widely different effects from
those of any other electrode materials. Townsend,* for
instance, illustrates the lowering of both sparking potential
and the "normal" cathode fall by means of them. Attention
was no doubt originally directed to them after aluminum,
magnesium and other alkaline-earth materials were found
to have some value for these purposes. Yet the alkalis
were available only with difficulty, in amalgams or by
electrolysis, and early data were wholly uncontrolled,
since methods of preparation, evacuation of the containing
vessel and purification of the working gas were undeveloped.
The vapor pressures and adsorption characteristics have
been carefully observed only in the past few years.

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*5, p.408

The analysis of Holst and Obsterhuis, while not complete, is the fullest and truest published for the gaseous breakdown phenomena.

$$\left| \qquad \cdot \quad \begin{array}{c} \cdot \\ \cdot \\ \cdot \\ \cdot \end{array} \qquad\qquad\qquad\qquad \right|$$
$$2 \qquad 2^2 \qquad\qquad\qquad\qquad 2^g-1$$
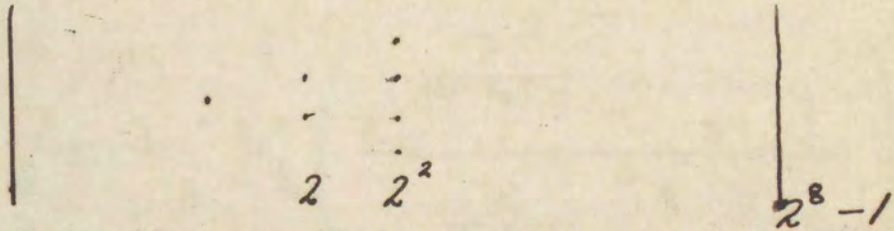
Let us consider one of the residual electrons in a gas before a discharge passes in it. In traversing the electrode space through a fall of electrical potential $V(=gVi$, where Vi is the ionization potential), the electron gives rise to a cumulative action. The number of positive ions (equal to that of electrons) grows at each collision distance $(\frac{V}{Vi})$ by a power of 2. These all (2^g-1) return to the cathode, from whence they may pull an electron if $(2^g-1)W \quad 1$ where $W \ (=f(\varphi)=f$ of the work function for the cathode) is the probability of the positive ion causing this act. Then the discharge will continue.

Magnesium in neon will allow this since $W=\frac{1}{63}$ when $g=6$; an alkali metal causes $W=\frac{1}{15}$ when $g=4$, these being conditions at minimum breakdown potentials.

This simplest analysis can apply only where the collisions are elastic; i.e., where the gas is rare. Such conditions are the only interesting ones for the present case where constancy of conditions over long periods, hence lack of

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chemical reaction, is desired.

In general

$$V = V_i K \left(\frac{e^{\frac{K}{430 \lambda_n T_8}} + 1}{e^{\frac{K}{430 \lambda T_8}} - 1} \right)$$

where

$$K = 273\, a p \sqrt{2x}$$

a = electrode separation

p = gas pressure

$x = 2\frac{m}{M} = 2 \times \left(\frac{\text{electronic mass}}{\text{gas molecule "}} \right)$

λ_n = mean free path

In neon

$$V = 42.5\, pa \left(\frac{e^{3.85 \frac{pd}{8}} + 1}{e^{3.85 \frac{pd}{8}} - 1} \right)$$

VanVoorhis* recently published some careful com-
parisons on the sparking potentials between pure aluminum
and potassium-coated aluminum electrodes:

MINIMUM SPARKING POTENTIALS

	He	Ne	Ar
Al	147 V.	168 V.	192 V.
K-coated Al	77.5	74.6	70

GENERAL LAW OF VARIATION WITH GAS PRESSURE (p) AND ELECTRODE SEPARATION (d)

Al	127*.57 pd	149*.50 pd	173+1.6 pd
K-coated Al	70+.31 pd	68+.33 pd	58+2.3 pd

These data illustrate the magnitude of effect, which is similar in the case of "normal" cathode fall. Continued study of the phenomena is amply justified not only by the improvements in technique and purity of materials for further usefulness, but by the aid which the correct data must lend to our knowledge of the alkalis, adsorption, etc. Moreover the problems of preparation and distribution of the alkalis, entailed in a device for considerable commercial use, are physico-chemical problems of wide interest. Hackspill has actively developed the methods of alkali metal prepara-tion used in the present work, improvement having been devised by members of the General Electric Company Research Laboratory. The first method used, typically, $Ca+2NaCl$ $CaCl_2+Na$, was described in 1913[8]. The method using CaC_2, hydride, or silicate, was described in a British patent in 1921[9]. Hackspill further patented a method using $Na_2Si_2O_3+FeSi_2$ at $800°-1000°$. These methods were all used in relatively low vacuum and the metal was redistilled. The present use must permit of a high vacuum in the tube, the rare gas filling necessitating just as high a vacuum as that in a tube which is to remain permanently evacuated. The first or chloride method is best adapted to the purpose and has been used, although the merits of all will be considered.

APPARATUS

The use of alkalis will be studied in a specific type of tube used for voltage regulation purposes, known as the UX 874. The desirable characteristics are

1. Low breakdown voltage (125 V.)

2. Maintenance of a voltage drop of 90 V. for currents of at least the range 0-60 m.a.

3. Preceding characteristics to be independent of temperature, period of operation, vibration, etc.

4. Long life ($>$1500 hours)

5. Freedom from irregularities, such as sudden small fluctuations of characteristics

A later design is shown in Fig. 1. A nickel cylinder of .010" material 1" in diameter and 1-1/4" long occupies a central position in a glass bulb of the ordinary lamp size. A .050" nickel wire protrudes through an alumina insulator syrmounting a glass stem, the small wire being in the center of the cylindrical outer electrode (cathode) space. This wire is the anode. A small nickel pellet carries the reactants to form the alkali metal, which deposits upon the bulb.

A high quality high vacuum system is used for exhaust as shown in Fig 2, with the addition of a gas supply bulb. This system is used in the laboratory, and slightly different arrangements in the factory.

The materials used in the production of alkali will

be described. LiCl, NaCl and KCl, as well as RbCl,
were c.p. materials from supply houses. CsCl was
obtained from Maine pollucite ore, and finally by pre-
cipitation as a double salt with $SbCl_3$ and removal of
Sb by precipitation with H_2S. Calcium was prepared by
electrolysis of fused chloride with some bothersome
variations in purity.

Manufacture of a tube consists of assembly of
parts previously heated to high temperature in a hydrogen
atmosphere, evacuation of the tube with an oven bakeout
at temperatures from 280-350° C, followed by thorough
heating of the cathode with a high frequency furnace. Then
the alkali is produced by heating its pellet with the
furnace. The new thoroughly exhausted bulb is filled with
about 10 mm of the working gas and sealed off the pump.
There follows an ageing process on alternating current
(approximately 200 milliamperes from a 110 V. AC line) until
constant characteristics result. Tests are made after
24 hours' operation, and again after another 24 hours of
inactivity. It is well to note that in careful work the
alkali was produced in an adjoining small tube from which
it was redistilled, hence purified, into the bulb used.

Measurements of operating bulb temperatures were first
made with mercury thermometers held with putty. Final measure-

ments were made with the thermocouple arrangements shown
in Fig. 3.   That the latter measurements are more precise
is evident from the fact that higher temperatures were
reached and that the thermal conductivity of the metal
could permit variations from actual temperatures of the
order of .1° C. only.

RESULTS

A. Method of Alkali Preparation

Alkali metal chlorides and calcium have been used
throughout in the reaction mentioned. Caesium carbonate
produces a faster reaction than the chloride, so that the
operator cease heating the pellet as soon as he sees
metal deposited on the walls. The chloride reaction re-
quires him to observe an end of deposition as he continues
to heat the pellet, and this is difficult to estimate in an
obscured bulb. The carbonate method however produces more
foreign gas (CO_2) and its advantage is not unqualified.

Further data will be taken on the temperature of the
reaction for the different alkalis (with pyrometer, etc.),
but for most purposes the following data suffice:

	Pellet T at which metal appears	Max T	Time at max. until no more metal is visibly produced	Yield
Cs	500° C.	600°	10 sec.	Complete
Rb	800°	1000°	30 "	"
K	1000°	1500°	1 min.	90%
Na	1200°	1500°	2 "	50%
Li	1500°	1500°		Barely visible

The maximum feasible amount of chloride is 150 mg. The following table demonstrates the theoretical yield from the standard charge:

	Molecular Wt.	gm. equiv.	Max. yield of alkali (gm)
LiCl	42.5	.00353	.0247
NaCl	58.5	.00256	.059
KCl	74.5	.00201	.0786
RbCl	120.9	.00124	.106
CsCl	168.5	.00089	.118

AGEING

For any of these tubes with gas fillings an optimum aging time exists for a given rate, and the optimum time is determined by the type of tube. The curve of Fig. 4 demonstrates what common sense will verify - that with a clean-up of impurities comes a decrease in breakdown and regulation potentials, until such time as the working gas itself is cleaned up. It is found that a rubidium filled tube reaches the optimum state (for similar aging rates) much sooner than a caesium tube. Times of aging vary by several hundred percent.

ELECTRICAL CHARACTERISTICS

The electrical characteristics of tubes varied only as to alkali content are summarized in the following table. The gas filling in each case was 10 mm of the "natural" Ne-He mixture (75% Ne, 25% He) with 250 microns of argon.

Alkali Metal	BD voltage	"Cold" Regulation voltage	BD voltage	"Hot" Regulation voltage	Test Number
Lithium	160	142	164	163	RG27
Sodium	126	87	138	108	RM82
Potassium	93	75	97	66	RCM93
Caesium	105	76	93	70	RCM96
ium-Potassium	97	71	105	76	RG45

Direct Comparison

	BD voltage	Regulation voltage	BD voltage	Regulation voltage	Test Number
Sodium	150	85	152	83	
Potassium	124	70	110	90	RCM75
Caesium	90	65	90	70	
Sodium	104	74	105	77	RCM75
Potassium	87	80	82	75	
Caesium	91	73	82	65	+ 250

A test for effect of bulb size

Potassium	BD voltage	Regulation voltage	BD voltage	Regulation voltage	Test Number
(large 250cc)	90	55	82.5	61	
(small 75cc)	93	75	97	66	RCM93

Typical Variations

(Sodium in six tubes of RM-82)

	Cold		Hot	
	BD	Reg.	BD	Reg.
1	107	90	151	113
2	124	82	139	102
3	145	95	152	115
4	135	84	134	112
5	123	84	123	105
6	125	89	127	100
Average	126	87	138	108

Each value given in comparison of the alkalis is an average, such as is shown in the last table of "typical variations". The characteristics of a single tube are derived from the averages of several determinations following the ageing period.

The effect of increasing the current passing in the tube above the normal value is demonstrated in the table and Fig. 4 b. Data were taken with latest design of caesium filled tube (S 21).

Current (ma.)	Voltage	BD Voltage	Wattage	
10	91	118		Characteristics taken with maximum speed. Total time for this increase and decrease of load = 1 minute.
50	94			
100	96			
200	98.5			
250	100			
300	101.5			
400	103-90			
300	88.5			
250	87.			
200	86			
100	84.5			
500	53.0		26.5	Being Equilibrium Readings at each point.
400	62.5	95	25.0	
325	76		24.7	
225	84	100	18.9	
75	87.5		6.6	

TEMPERATURE DETERMINATION

Now since the electrical data demonstrate in some cases considerable difference between the "hot" or "operating" and the "cold" or "idle" characteristics, it became of interest to discover whether this was inherent in the case of alkalis and whether it was simply correlated with the change in vapor pressure.

The best improved tubes available were chosen for tempera-

ture tests; namely, two with caesium and two with rubidium.
Two effects were notable--an increase in breakdown and regu-
lation voltages due to operation at lower than normal bulb
temperatures (especially marked in the rubidium tube), the
rapid attainment of equilibrium, the time of readjustment
to a changed condition corresponding only to a thermal rate.
The tables and Fig. 5 demonstrate the pronounced effect upon
rubidium tubes as against caesium. Undoubtedly other alkalis
will give rise to larger differences. Yet the constancy of
characteristics with Cs or Rb is ample for practical purposes.

Effect upon B D Voltage

Ambient Temperature °C	0	24	50	75	100
CCM 120-3	109	103	107		
CCM 120-4	115	108			111
CC 116-2	130	110	113		116
CC 117-2	138	115	112	114	114

Effect upon regulation voltage

CCM 120-3	91	89	87		
CCM 120-4	91	92			95
CC 116-2	108	93	92		99
CC 117-2	114	91	90	89	95

Effect of operating rubidium tube 117-2 at 0°C

Time (minutes)	BD	$V_{10 m.a.}$	$V_{50 m.a.}$	
0	116	89	94	
5	119	96	101	
10	122	103	108	
15	131	104	113	
20	130	110	118	
25	138	109	116	Idle since 20 min point.

Temperature distribution over the glass bulb was determined with the very small thermo-couple arrangement described. This distribution varies with the opacity of the bulb. A bulb well lined with alkali metal will reflect heat into all parts of the bulb, and indeed is found to have a more uniform temperature than a partially clear bulb. For positions numbered in Fig. 3 the temperatures found are as follows:

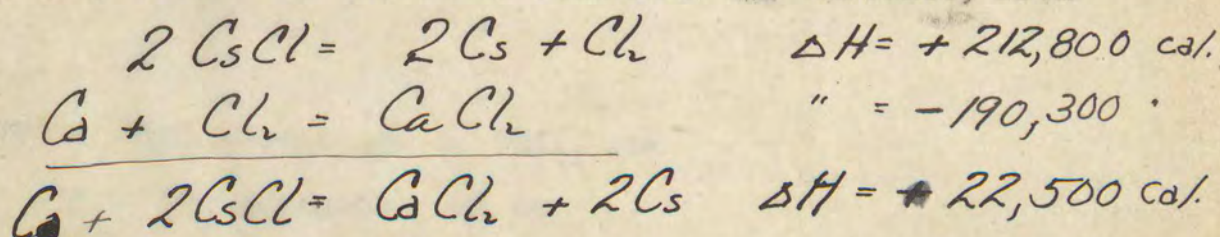|	①	②	③
Half clear bulb 147-6	51	47.5 43.5	37
Very Opaque bulb	40	46	39

4.5 watts are consumed in each tube from the electrical circuit, operation being at a normal 24° C. room temperature.
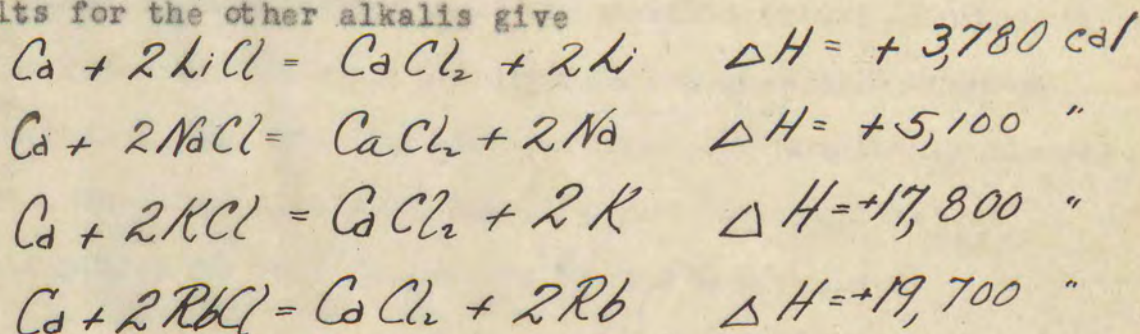
DISCUSSION OF REACTION

Now the reaction used for formation of the alkalis is not susceptible to precise treatment with the available data. I at first considered that it would be possible to treat the equilibrium constant with complete vapors pressure data. Yet in the first place the reaction is not entirely between gases; and too there are no data on the vapor pressure of dry calcium chloride. That the reaction is not entirely a gas reaction is shown by its progress in the pellet. Spots darker than the surroundings suddenly appear and travel at random about the pellet until no more alkali metal appears on the walls of the tube. Some metal is produced, too, when in the process of

heating the cathode the pellet temperature rises, but not to
a visible temperature.   It is to be expected then that the
equilibrium is favorable at temperatures at least as low as 700° C.
and that either the equilibrium constant or the speed of reaction
rises rapidly as the temperature rises to 5100° C.

Now the heat of this reaction can only be estimated at
room temperature for the solid reaction. For instance, from

$$2\,CsCl = 2\,Cs + Cl_2 \qquad \Delta H = +\,212,800 \text{ cal.}$$
$$\underline{Ca + Cl_2 = CaCl_2 \qquad\qquad " = -190,300 \text{ .}}$$
$$Ca + 2CsCl = CaCl_2 + 2Cs \qquad \Delta H = +\,22,500 \text{ cal.}$$

Results for the other alkalis give

$$Ca + 2LiCl = CaCl_2 + 2Li \qquad \Delta H = +\,3,780 \text{ cal}$$
$$Ca + 2NaCl = CaCl_2 + 2Na \qquad \Delta H = +\,5,100 \text{ "}$$
$$Ca + 2KCl = CaCl_2 + 2K \qquad \Delta H = +\,17,800 \text{ "}$$
$$Ca + 2RbCl = CaCl_2 + 2Rb \qquad \Delta H = +\,19,700 \text{ "}$$

Now at room temperature ΔC_p for the caesium reaction is

$$C_{pCaCl_2} + 2\,C_{pCs} - C_{pCa} - 2\,C_{pCsCl}$$
$$= 18.22 \quad +16.0 \quad -7.0 \quad -25.2 \quad = 2.2 \text{ cal.}$$

There are no data on the specific heats of the reactants to
permit calculation of the data for temperatures used, to say
nothing of the data on heats of evaporation; but there are rather
complete data for these reactions in melts over lead. Jellinch
and Czerwinski[8] found agreement between purely chemical and
electrochemical methods for the equilibrium. The alkali and

alkaline earth metals are soluble in lead whereas the salts
are not. Although they found the temperature coefficients
of the equilibrium constant small, their data were taken
at 1000° C. and hence approximates the conditions of our
practice. When expressed in mol-percentage the reaction

$$2 Na + CaCl_2 \longrightarrow 2 NaCl + Ca$$ has a constant

$$\left(\frac{100-y}{y}\right)\left(\frac{x}{100-x}\right) = K = .21$$
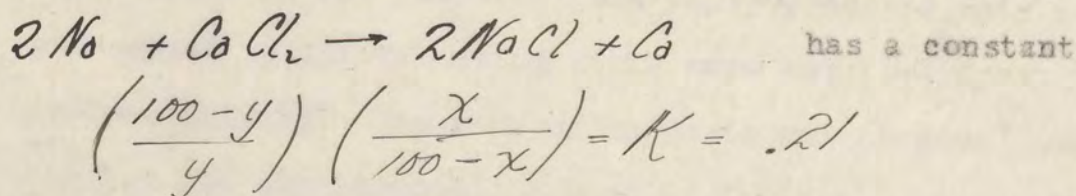
where x = mol percentage of $CaCl_2$ and

      y = atom percentage of Ca

They found a changing order of the alkalis in the electro-
motice force series with the increases temperature. Indeed
the metals K, Na, Ba, Ca, Sr, approach each other very closely.

      Now, the applicability of a gaseous equilibrium
consideration to these reactions should be examined.

Substance	melting point	boiling point
Cs	28.5	670
K	62.5	712
Rb	39.	696
Na	97.9	750
Li	179.	1400
Ca	785	—
CaCl_2	780	900 probably
CsCl	645	1303
RbCl	715	1410
KCl	775	1417
NaCl	800	1439
LiCl	614	1360

The table demonstrates that the reaction may well take place in the liquid phase as the reactants all melt at less than 900°C. The residue is not a fused mass, however, when opened in air, a fact which may be explained by the great agitation during the escape of the alkali.

The hypothesis that the reaction takes place in the vapor phase is not tenable. The vapor pressure data as summarized in the following table were compiled from various sources. The work of Langmuir and Kingdon[10] on caesium was supplemented by that of Killian[11] on rubidium; and collected data of Landolt--Bornstein[4] on sodium supply the essential alkali data. There are no data on lithium. Calcium data have lately been critically revised by Dr. Jones[12], and the data on chlorides are derived from Walker and from my computation from Landolt--Bornstein.

$$\log_{10} p(bars) = A - \frac{B}{T}$$

The ratio p_{cs}/p_{ca} is given by $\log p_{cs}/p_{ca} =$

$$\left(10.65 - \frac{3992}{T} - 15 + \frac{12750}{T}\right) = -4.35 + \frac{8758}{T}$$

At 300°K for instance this logarithm would be 29.2. At 1000°K the logarithm becomes, however, 4.4. At least for this range of temperature we could wellneglect the pressure of Ca as compared with Cs. CsCl and $CaCl_2$ both possess pressures for a low order too. Hence we could write for a vapor phase equilibrium

$$\Delta F = -RT\ln K_p = -2 RT\ln p_{cs}$$

Then considering the vacuum under which we work to be 1 bar,

Substance	A	B	Reference
Cs	10.65	3992	10
Rb	10.55	4132	"
K	11.83	4964	"
Na	9.86	4875	Own calculation
Ca	15.0	12750	Jones-Lewis
CsCl	11.19	8170	13
RbCl	10.998	8260	"
KCl	11.53	9150	Own calculation
NaCl	11.22	9260	" "
LiCl	10.92	8130	13

this reaction would run to $\ln p_{cs}$ 0 $10.65 - 3992/T$.
This is at a temperature of $375°K$. At this temperature
the rate of evaporation of Cs would be $43.74 \times 10^{-6} \sqrt{\dfrac{132.8 \times 1}{375}} =$
$$26. \times 10^{-6} \text{ gms/sec. cm}^2$$

Now no Cs is produced during long (15-30 min.) bakeout at
temperatures as high as $600°K$ where both equilibrium, dif-
fusion, and rate of evaporation would be much more favorable.
Our conclusion must be that the reaction is not occurring in
the vapor phase.

The fact that the reaction occurs about random centers ,
which centers move rapidly about the pellet during reaction,
lends great support to the hypothesis of liquid phase reaction.
The centers are probably xxx solid Ca, although at the higher
temperatures (in the Li reaction, for instance) the liquid
must be fairly homogeneous with molten Ca.

Let us consider the energy relations in the typical
reaction

$$Ca + 2 NaCl \longrightarrow CaCl_2 + 2 Na \qquad \text{since data are}$$
rather complete for it.

$$\Delta H_{298} = 5100 \text{ cal.} \quad (\text{solids})$$

Now $\Delta F_{298} = \Delta H_{298} - T \Delta S_{298}$

Estimating S_{298} for $CaCl_2$ by Latimer's rule

$$S_{CaCl_2} = \begin{array}{l} 3/2 \text{ R ln } 40.07 - .94 = \quad 10.64 \\ +2 \times 3/2 \text{ R ln } 35.46 - .94 = \underline{19.32} \\ = 29.96 \end{array}$$

$2 \, S_{Na} \text{ (solid)} = 24.4 \qquad S_{Ca} \qquad 10.64$

$S_{CaCl_2} \qquad = \dfrac{29.96}{54.36} \qquad 2 \, S_{NaCl} \qquad \dfrac{34.8}{45.44}$

19.

Hence, $\Delta S_{298} = 54.36 - 45.44 = \quad + 8.92$
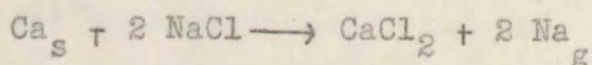
$$\Delta F_{298} = 5100 - (298 \times +8.92) = 2440$$

Now $\quad \Delta F$ for the process $2\ Na_s \longrightarrow 2\ Na_g$

is $-2\ RT\ \ln \dfrac{10^{-12.49}}{1} \quad = 2(-593 \times 2.303 \times -12.49)$

$$= 2(17050)\ cal.$$

$$= 34100\ cal.$$

Hence for the reaction

$$Ca_s + 2\ NaCl \longrightarrow CaCl_2 + 2\ Na_g$$

ΔF is $2440 + 34,100 = 36540\ cal.$

For this last process

$\Delta S = (70.12 + 29.96) - (10.64 + 34.8) \qquad = 54.64.$

$\Delta H = \Delta F + T\Delta S = 35400 + 54.64 \times 298 \qquad = 52820\ cal.$

Now $\quad \Delta H = \Delta H_o + \Delta C_p \times T$

$C_{pCa} = 6.4 + .001\ T$ for range

$C_{p\ 2NaCl} = 25.6$

$C_{p\ CaCl_2} = 18.22$

$C_{p\ 2Na} = 10$

Hence $\Delta C_p = 28.22 - (32.0 + .001\ T) \quad = -3.78 - .001T$
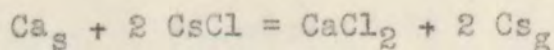
$\Delta H_o = 52820 + 3.78\ T + .001\ T^2$

$$= 52820 + 1125 + 90 \quad = 54035$$

$\Delta F = 54035 + 3.78\ T\ \ln\ T + .0005\ T^2 + 1\ T$

$$I = \frac{36540 - 54035 - 6400 - 45}{298} \quad = \frac{-23940}{198}$$

or $I = -80.5$

A similar calculation gives for

$$Ca_s + 2\ CsCl = CaCl_2 + 2\ Cs_g$$

$$\Delta H_{298} = 43,350$$

$$\Delta F_{298} = 23,150$$

$$\Delta H = 44,470 - 3.48\ T - .001\ T^2$$

$$\Delta F = 44,470 + 3.48\ T \ln T + .0005\ T^2 - 91.6\ T$$

The reaction probably is between CsCl vapor and Ca solid at the lower temperatures; without doubt becoming a reaction between Ca solid and CsCl liquid above $645^\circ C$. At $600^\circ K$ approximately the lowest temperature for production of Cs, $p_{Cs} = 10^4$ bars, $p_{Ca} = 10^{-6}$ bars.

$$p_{CsCl} = 10^{-2}\ \text{bars.}$$

The compounds $CaCl_2 - LiCl$ (492°), $CaCl_2 \cdot 4\ NaCl$ (580°), $CaCl_2 - KCl$ (754°) may complicate the reaction; but at least in the Cs reaction practically quantitative completion results.

At least we may bear in mind this result of thermodynamic reasoning, that this reaction will run more easily as the pressure is lowered.

It is instructive to calculate the rates of evaporation of the resultant alkali. Now the estimated rate of evaporation of Cs at a temperature not far above $900^\circ K$ is .1 gram per sec. from a pellet whose available openings do not average over 1 sq. mm., or a rate of 10 grams / sec. $(cm)^2$. The whole yield of caesium may be seen to condense practically instantaneously after the first deposit on the walls.

Langmuir's formula gives

$$m(\text{gms per sec}) = 43.74 \times 10^{-6} \sqrt{\frac{M}{T}} \; p(\text{bars})$$
$$= 43.74 \times 10^{-6} \sqrt{\frac{M}{T}} \; 10^{A - \frac{B}{T}}$$

Substance	M	$(43.74 \times 10^{-6} \sqrt{M})$	$m(900°K)$	$p(900°K)$
Cs	132.8	504×10^{-6}	27.7 gm.	1.65×10^{-6} bars
Rb	85.5	404 "	12.25 "	90 " "
K	39.8	273	18.9 "	2.09 " "
Na	23.0	210	.194	.28 " "
Li	6.94	115	.00326	.00085 " "

This method of studying a reaction might be very fruitful, it seems to me. Input from a high frequency furnace to a pellet in vacuum can be accurately known, the rise of temperature followed with a pyrometer, the rate of reaction measured with a stop watch, and the products readily analyzed.

The carbonate reaction

$$Cs_2CO_3 + Ca \longrightarrow CaO + CO + 2Cs \qquad -28,330 \text{ cal.}$$
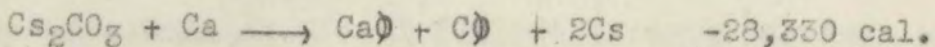
will very possibly remove the CO_2 at such a rate as materially to improve the speed over the chloride reaction. At least it is faster and occurs at comparable temperatures.

In order to correlate the phenomena of the tube with the properties of the alkalis an estimate of the cathode temperature must be made. Direct determination is difficult;

the temperatures are not high enough for pyrometry,
with which the cathode glow would interfere, in any
case.   A thermocouple is likely to be affected by its
action as a collector of ions and give false readings.
. hence we must resort to calculation.

Addenda to Reaction Discussion.

Diffusion: A high temperature coefficient for the
typical reaction would be indicated by the large tem-
perature coefficient of diffusion; particularly in the
liquid reaction $Ca_s + 2 CsCl_l \longrightarrow CaCl_{2\ s} + 2 Cs_g$

This coefficient may be from 30% to 100% per $10^{\circ}C$ rise
of temperature to judge from the meager data of Taylor,
for diffusion of $CsCl_l$ to, and Cs_g away from, the
reacting layer.

Alloying: Mellor states that little alloying takes
place between the alkail metals Cs, Rb, K. Hence, the
presence of a mixture of chlorides will only result in
production of the mixture of alkali metals.

Now the discharge in the tube causes practically the whole potential drop to occur within 1 mm of the cathode[19]. Here the energy dissipation of the tube occurs. Not all of it is a bombardment of the cathode. Without doubt the temperature of the gas just outside the cathode is the highest in the tube. Whether this be so or the cathode itself be hottest, is immaterial to our calculation. Under standard conditions an upper limit to the cathode temperature may be set by a calculation assuming conduction alone from the outer surface of the cylinder.

$$\text{Thermal conductivity of He} = .34 \times 10^{-3} \frac{gm. \, cal}{cm-sec-°C.}$$

$$" \qquad " \qquad " \quad Ne = .12 \times 10^{-3} \quad "$$

$$" \qquad " \qquad \begin{array}{l} \text{of a mixture} \\ \begin{cases} 75 \, Ne \\ 25 \, He \end{cases} \end{array} = .18 \times 10^{-3} \quad "$$

Now the Smoluchowski *21 formula for such a case in a gas at low pressure gives

$$W_c = \frac{2\pi H \, l \, \Delta T}{\log_e \frac{r_o}{r_1} + \delta \left(\frac{1}{r_1} - \frac{1}{r_o} \right)}$$

when $\qquad$ H = thermal conductivity

l = length of cylinder

r_0 = radius of glass wall

r_1 = radius of cylinder

γ = a function of the mean free path which in this case is comparable to hydrogen $\qquad$ for which γ = .008

Then $\Delta T = \dfrac{4.5}{\dfrac{2 \times 6.28 \times .18 \times 10^{-3} \times 5}{.69 + .008 \left(\dfrac{1}{1.25} - \dfrac{1}{2.5}\right)}} = 270°C.$

Checking back, with the assumed temperature difference to the walls, the leads (2 in number) can account for but a small part of the loss

$W_{leads} = 2 \times \left(\dfrac{.142 \times (270 + 25) \times .050}{7.5}\right) = 2 \times .28 = .56 \text{ watts}$

Hence an upper limit of cathode temperature is 250° C. rise above the walls. Now the walls are at 21° C. above the room and there is a drop of 2° C. in the glass wall.

Since $\Delta T_{glass} = \dfrac{4.0}{\dfrac{125 \times .0015}{.1}} = 2.1°C.$

An absolute maximum of temperature rise for cathode above surrounding temperature is then 275° C. at 4.5 watts.

We shall assume that when the effect of convection from

within the cylinder is weighed the temperature rise is 200° C. at 4.5 watts and that this temperature rise is proportional to watts input.

This result checks well with our data on overload, which show an arc at about 25 watts or a probable temperature of 1000° C. at equilibrium. Under these conditions the bulb temperature rise will be 125° C. and the existing Cs vapor pressure about 15 bars. Thermionic emission will be expected at these temperatures to cause an arcing.

— — —

Electrical characteristics show the phenomena due to alkali to be variable with temperature, excepting in the case of caesium. The variability increases as we pass from rubidium to potassium to sodium. Kingdon finds the complete film of caesium on tungsten to be broken at about 700° K. Undoubtedly on nickel this adsorption would be considerably less firm, its work function being less than tungsten's. We find it reasonable then that our electrical breakdown voltage, abnormally low because of a film of caesium, should begin to increase at 425° C. and that rubidium should show a consistent increase of 10 volts in breakdown voltage for a cathode temperature of 200° C.

Moreover this effect is accentuated by the removal of
alkali metal by gaseous bombardment of the cathode. Kingdon
finds removal of onethorium atom for each 100 neon positive ions
striking with 80 V. energy. Even greater amounts of caesium
will be removed by the same forces. This bombardment effect
is intimately related to the disappearance of the working gas,
so that relatively slight improvements, such as the use of
caesium instead of potassium, increase the life of the tube from
50 hours to 1500 hours.

THE ACTIVITY OF ALKALIS AS GETTERS

The ageing period for caesium tubes is shorter than for
other alkali tubes. Many tubes show a development of the
white deposited oxide or similar compounds during this period,
always correlated with the known presence of impurities
originally. The amount of alkali present is sufficeint to
clean up externally large amounts of reactive gases - as for
instance 20 cc of oxygen at atmospheric pressure (=.002 gm
equivalents). Many reactions (for instance with nitrogen)
must owe their success to the presence of the discharge. A
fruitful research would undoubtedly result from a comparison
of aging rates at like bulb temperatures as maintained by a
furnace and as maintained by the discharge. Water vapor will
be promptly decomposed with the formation of oxides and hydrides

or absorbed in hydration of the oxide. When the usual order of impurities remains (at pressures certainly not greater than 1 bar) and there exist so many methods by which reaction may take place to remove them from the space, the efficiency of the alkali getter may be understood. Reaction may proceed with the metal, the oxide, the carbonate or any of several compounds present when impurities are being cleaned up. Rusk notes large absorption of hydrogen in a potassium vapor discharge, a typical phenomenon. The alkalis, which serve as catalysts for so many reactions, no dount catalyze the reactions of their own compounds too.

SUMMARY

The alkali metals have been studied for vapor pressures, for adsorption on a nickel surface at ordinary temperatures, for their ease of removal by bombardment of positive ions, and for their effect upon the glow discharge in inert gases.

The metals caesium and rubidium have essential advantages for the application which prompted the research over the other metals.

1. They have desirable maximum effects upon electrical characteristics at room temperature.

2. They do not cause appreciable temperature variation in those characteristics (Indeed our conclusion must be that any alkali is efficient to its maximum in lowering the characteristic voltages so long as the cathode surface has at least a monomolecular film of the metal upon it.)

3. They are more effective getters.

4. The anomalous behavior of K with respect to vapor pressure and in its glow discharge character- istics approaching nearer Cs than Rb, correlates with the anomalous behavior at high pressures found by Bridgman.[20]

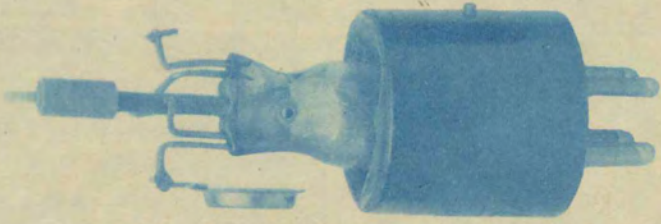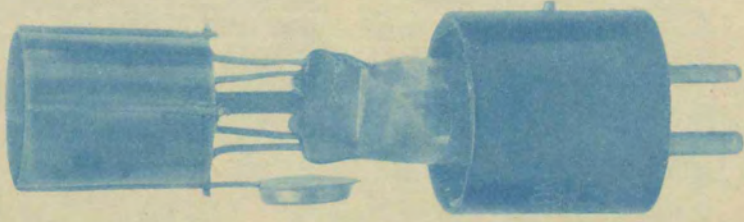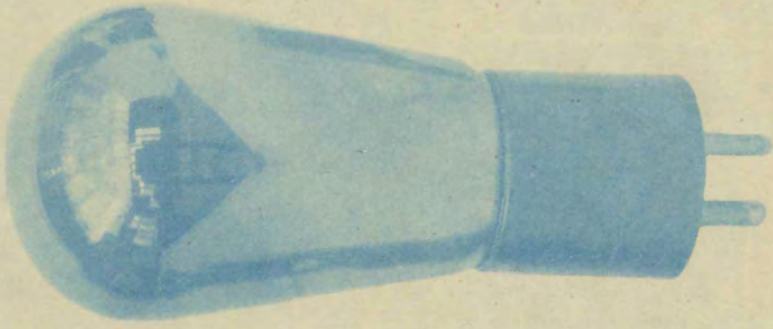The reactions typified by

$$2CsCl + Cd \rightarrow CdCl_2 + 2Cs$$
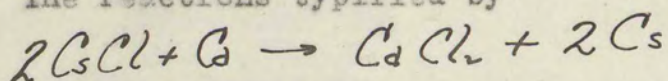
have been studied for equilibrium and kinetics.

Extension of this work is to be considered very ffuitful in the following directions.

1. More exact correlation of electrical effect with adsorption and vapor pressure data, particularly by the precise investiga- tion of cathode and gas temperatures.

2. Extention of the method used in studying reaction of forma- tion by more exact measurements.

3. Extension of thermodynamic theory to the cathode phenomena.

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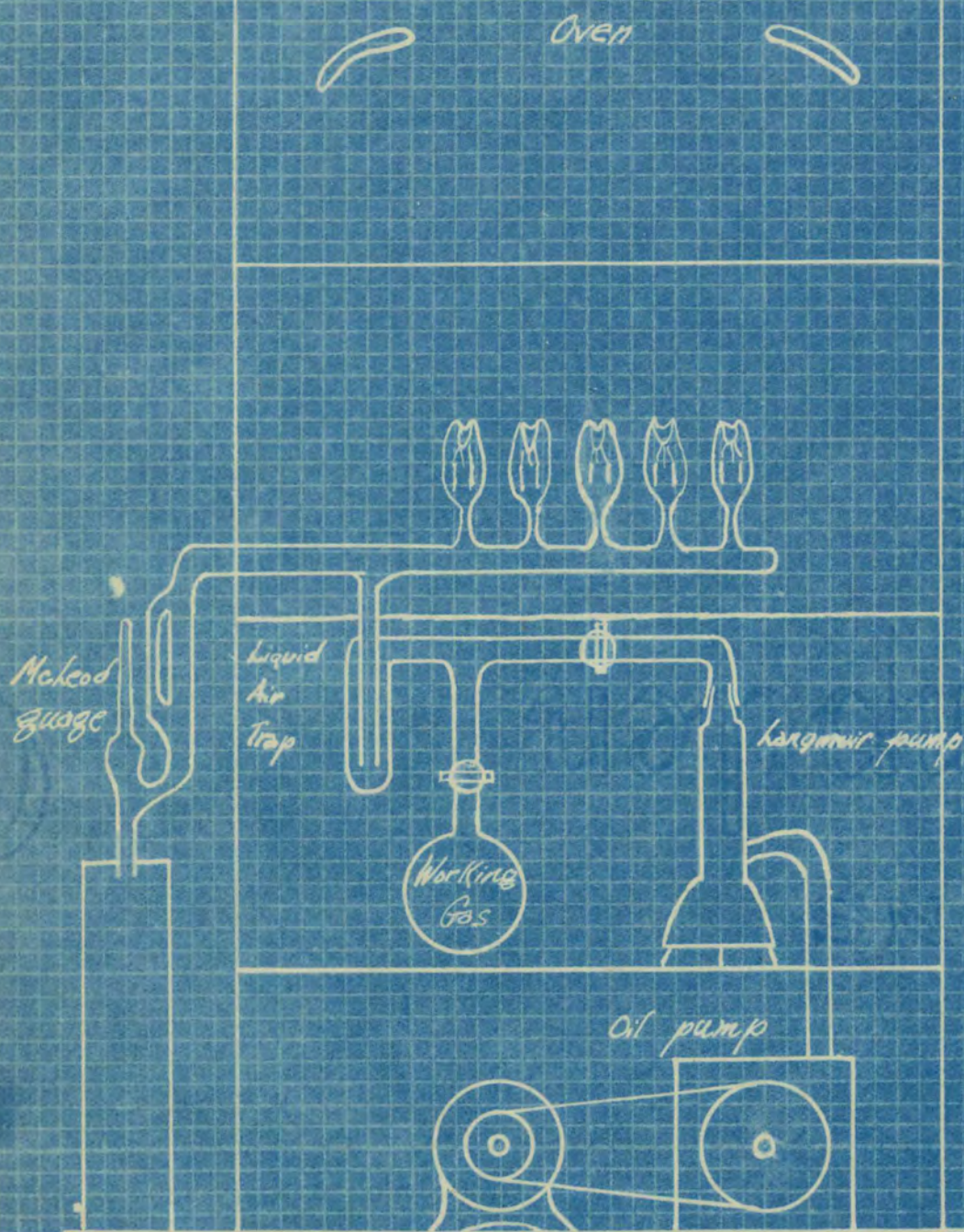21. General Electric Review - H.A.Jones, Sept. 1925, p. 654

RADIOTRON MODEL UX874 REGULATOR TUBE.

INDEX 654

10 14 25

432800

Fig 2.

Oven

McLeod Guage

Liquid Air Trap

Working Gas

Langmuir pump

Oil pump

H 3606552

L C Lewis
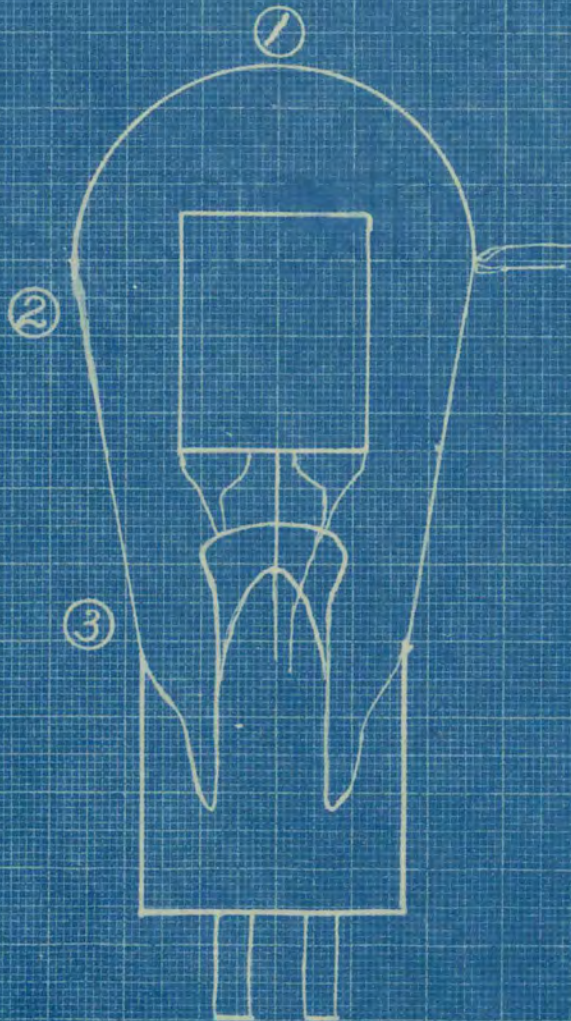
System for evacuation and gas filling of
alkali metal- rare gas glow tubes.

Fig. 3.

*Tube and
thermocouple
arrangement.*

H3606553

h. C. Lewis

Fig 4 d.
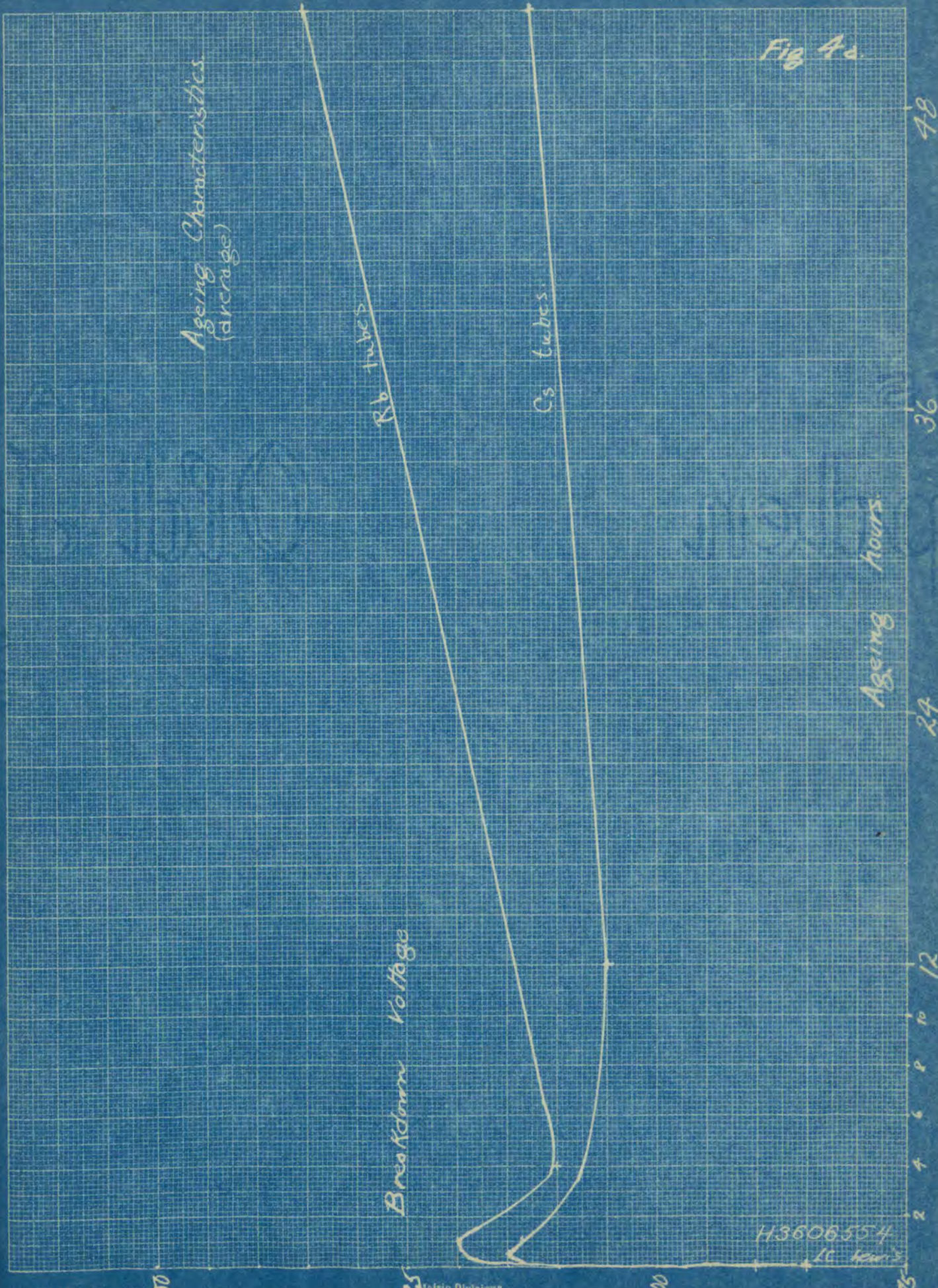
Ageing Characteristics.
(average)

Rb tubes

Cs tubes

Breakdown Voltage

Ageing hours

48

36

24

12

H3606554

Fig 46

Regulation

Regulation
Voltage

Breakdown

Breakdown
Voltage

—120

—100

—80

Equilibrium Electrical Characteristics
vs.
Watts and
Estimated Cathode Temperature

Dotted lines = instantaneous
characteristics

H 3606555

Estimated Cathode Temperature

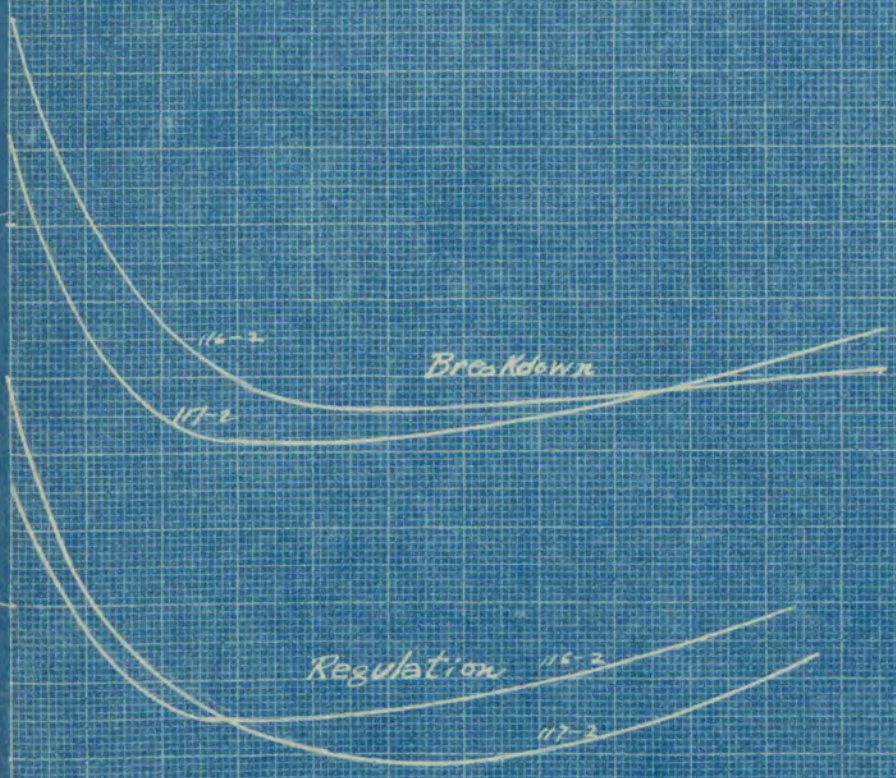400   800   1000   1200   A.C.Lewis

10   Watts   20   25   30

Fig. 5

Voltage

Electrical Characteristics
vs.
Ambient Temperature.

Breakdown

116-2

117-2

Regulation 116-2

117-2

Ambient Temperature °C.

H3606556

L.C. Lewis

0

50

Metric Divisions 100

150

FN-156 35m 10-8-43

Fig 6.

Vapour Pressures
of the
Alkali Metals

$\log_{10} p$ (bars) vs. $\frac{1}{T}$ (°K)

VAPOR PRESSURE
OF
Hg, Cs, Rb, K and Na.

J PAYNE
11/6/26.

H-3609058