Studies of alkali metals

Lester Clark Lewis

Union College - Schenectady, NY

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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 Department of Chemistry of Union College in partial fulfillment of the requirements for the degree of Master of Science in Chemistry by

Name  

Approved by  

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 encourages 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 observation 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 characteristics). 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 discharges 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.

*5, p.408
The analysis of Holst and Obsterhuis, while not complete, is the fullest and truest published for the gaseous breakdown phenomena.

\[ 2^2 = 2^2 \]

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 \( V(=gV_i) \), where \( V_i \) 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 \( \left( \frac{V}{V_1} \right) \) by a power of 2. These all \( (2^g-1) \) return to the cathode, from whence they may pull an electron if \( (2^g-1)W \) where \( W = f(\varphi) = \frac{F}{e} \) 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
chemical reaction, is desired.

In general

\[ V = V_i \left( K \left( \frac{e^{\frac{K}{430 N T_B}}} {e^{\frac{K}{430 N T_B}}} + 1 \right) \right) \]

where

\[ K = 273 a p \sqrt{2x} \]
\[ a = \text{electrode separation} \]
\[ p = \text{gas pressure} \]
\[ x = 2 \frac{m_a} {M} = 2 \times (\text{electronic mass}) \]
\[ N = \text{mean free path} \]

In neon

\[ V = 42.5 p a \left( e^{3.85 \frac{p a} {8}} + 1 \right) \]

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

**MINIMUM SPARKING POTENTIALS**

<table>
<thead>
<tr>
<th></th>
<th>He</th>
<th>Ne</th>
<th>Ar</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>147 V</td>
<td>168 V</td>
<td>192 V</td>
</tr>
<tr>
<td>K-coated Al</td>
<td>77.5</td>
<td>74.6</td>
<td>70</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th></th>
<th>Al</th>
<th>K-coated Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>p</td>
<td>127*.57 pd</td>
<td>149*.50 pd</td>
</tr>
<tr>
<td>a</td>
<td>70*.31 pd</td>
<td>60*.33 pd</td>
</tr>
</tbody>
</table>
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 preparation 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 → CaCl₂+Na, was described in 1913⁸. The method using CaC₂, hydride, or silicate, was described in a British patent in 1921⁹. Hackspill further patented a method using Na₂Si₂O₅+FeSi₂ at 800⁰-1000⁰. 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 alkalies will be studied in a specific type of tube used for voltage regulation purposes, known as the UX 974. 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 1, 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 precipitation as a double salt with SbCl₅ and removal of Sb by precipitation with H₂S. 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 250-350°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 now 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 ceases heating the pellet as soon as he sees metal deposited on the walls. The chloride reaction requires 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 \((\text{CO}_2)\) 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:
<table>
<thead>
<tr>
<th>Metal</th>
<th>Initial Temp.</th>
<th>Max Temp.</th>
<th>Time at Max.</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cs</td>
<td>500°C</td>
<td>800°C</td>
<td>10 sec.</td>
<td>Complete</td>
</tr>
<tr>
<td>Rb</td>
<td>800°C</td>
<td>1000°C</td>
<td>30 &quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>K</td>
<td>1000°C</td>
<td>1500°C</td>
<td>1 min.</td>
<td>90%</td>
</tr>
<tr>
<td>Na</td>
<td>1200°C</td>
<td>1500°C</td>
<td>2 &quot;</td>
<td>50%</td>
</tr>
<tr>
<td>Li</td>
<td>1500°C</td>
<td>1500°C</td>
<td></td>
<td>Barely visible</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Compound</th>
<th>Molecular Wt.</th>
<th>gm. equiv.</th>
<th>Max. yield of alkali (gm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiCl</td>
<td>42.5</td>
<td>.00353</td>
<td>.0247</td>
</tr>
<tr>
<td>NaCl</td>
<td>58.5</td>
<td>.00256</td>
<td>.059</td>
</tr>
<tr>
<td>KCl</td>
<td>74.5</td>
<td>.00201</td>
<td>.0786</td>
</tr>
<tr>
<td>RbCl</td>
<td>120.3</td>
<td>.00124</td>
<td>.106</td>
</tr>
<tr>
<td>CsCl</td>
<td>168.5</td>
<td>.00089</td>
<td>.118</td>
</tr>
</tbody>
</table>
AGING

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.
<table>
<thead>
<tr>
<th>Alkali Metal</th>
<th>BD Voltage</th>
<th>&quot;Cold&quot; Regulation Voltage</th>
<th>BD Voltage</th>
<th>&quot;Hot&quot; Regulation Voltage</th>
<th>Test Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lithium</td>
<td>160</td>
<td>142</td>
<td>164</td>
<td>163</td>
<td>RG27</td>
</tr>
<tr>
<td>Sodium</td>
<td>126</td>
<td>87</td>
<td>138</td>
<td>108</td>
<td>RM82</td>
</tr>
<tr>
<td>Potassium</td>
<td>93</td>
<td>75</td>
<td>97</td>
<td>66</td>
<td>RCM93</td>
</tr>
<tr>
<td>Caesium</td>
<td>105</td>
<td>76</td>
<td>93</td>
<td>70</td>
<td>RCM96</td>
</tr>
<tr>
<td>Lithium-Potassium</td>
<td>97</td>
<td>71</td>
<td>105</td>
<td>76</td>
<td>RG45</td>
</tr>
</tbody>
</table>

**Direct Comparison**

<table>
<thead>
<tr>
<th>Alkali Metal</th>
<th>BD Voltage</th>
<th>&quot;Cold&quot; Regulation Voltage</th>
<th>BD Voltage</th>
<th>&quot;Hot&quot; Regulation Voltage</th>
<th>Test Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium</td>
<td>150</td>
<td>85</td>
<td>152</td>
<td>83</td>
<td>RCM75</td>
</tr>
<tr>
<td>Potassium</td>
<td>124</td>
<td>70</td>
<td>110</td>
<td>90</td>
<td>RCM75</td>
</tr>
<tr>
<td>Caesium</td>
<td>90</td>
<td>65</td>
<td>90</td>
<td>70</td>
<td></td>
</tr>
<tr>
<td>Sodium</td>
<td>104</td>
<td>74</td>
<td>105</td>
<td>77</td>
<td>RCM75</td>
</tr>
<tr>
<td>Potassium</td>
<td>87</td>
<td>80</td>
<td>82</td>
<td>75</td>
<td></td>
</tr>
<tr>
<td>Caesium</td>
<td>91</td>
<td>73</td>
<td>82</td>
<td>65</td>
<td>+ 250</td>
</tr>
</tbody>
</table>

**A test for effect of bulb size**

<table>
<thead>
<tr>
<th>Alkali Metal</th>
<th>BD Voltage</th>
<th>&quot;Cold&quot; Regulation Voltage</th>
<th>BD Voltage</th>
<th>&quot;Hot&quot; Regulation Voltage</th>
<th>Test Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Potassium</td>
<td>90</td>
<td>55</td>
<td>82.5</td>
<td>61</td>
<td>RCM93</td>
</tr>
<tr>
<td>(large 250cc)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(small 75cc)</td>
<td>93</td>
<td>75</td>
<td>97</td>
<td>66</td>
<td></td>
</tr>
</tbody>
</table>
Typical Variations
(Sodium in six tubes of RM-82)

<table>
<thead>
<tr>
<th></th>
<th>Cold</th>
<th></th>
<th>Hot</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>BD</td>
<td>Reg.</td>
<td>BD</td>
</tr>
<tr>
<td>1</td>
<td>107</td>
<td>90</td>
<td>151</td>
</tr>
<tr>
<td>2</td>
<td>124</td>
<td>82</td>
<td>139</td>
</tr>
<tr>
<td>3</td>
<td>145</td>
<td>95</td>
<td>152</td>
</tr>
<tr>
<td>4</td>
<td>135</td>
<td>84</td>
<td>134</td>
</tr>
<tr>
<td>5</td>
<td>123</td>
<td>84</td>
<td>123</td>
</tr>
<tr>
<td>6</td>
<td>125</td>
<td>89</td>
<td>127</td>
</tr>
<tr>
<td>Average</td>
<td>126</td>
<td>87</td>
<td>138</td>
</tr>
</tbody>
</table>

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).
<table>
<thead>
<tr>
<th>Current (ma.)</th>
<th>Voltage</th>
<th>BD Voltage</th>
<th>Wattage</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>91</td>
<td>118</td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>94</td>
<td></td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>96</td>
<td></td>
<td></td>
</tr>
<tr>
<td>200</td>
<td>98.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>250</td>
<td>100</td>
<td></td>
<td></td>
</tr>
<tr>
<td>300</td>
<td>101.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>400</td>
<td>103.90</td>
<td></td>
<td></td>
</tr>
<tr>
<td>500</td>
<td>53.0</td>
<td>26.5</td>
<td></td>
</tr>
<tr>
<td>400</td>
<td>62.5</td>
<td>95</td>
<td>25.0</td>
</tr>
<tr>
<td>325</td>
<td>76</td>
<td></td>
<td>24.7</td>
</tr>
<tr>
<td>225</td>
<td>84</td>
<td>100</td>
<td>18.9</td>
</tr>
<tr>
<td>75</td>
<td>87.5</td>
<td></td>
<td>6.6</td>
</tr>
</tbody>
</table>

Characteristics taken with maximum speed. Total time for this increase and decrease of load = 1 minute.

**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 regulation 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

<table>
<thead>
<tr>
<th>Ambient Temperature °C</th>
<th>0</th>
<th>24</th>
<th>50</th>
<th>75</th>
<th>100</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCM 120-3</td>
<td>109</td>
<td>103</td>
<td>107</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CCM 120-4</td>
<td>115</td>
<td>108</td>
<td></td>
<td></td>
<td>111</td>
</tr>
<tr>
<td>CC 116-2</td>
<td>130</td>
<td>110</td>
<td>113</td>
<td></td>
<td>116</td>
</tr>
<tr>
<td>CC 117-2</td>
<td>138</td>
<td>115</td>
<td>112</td>
<td>114</td>
<td>114</td>
</tr>
</tbody>
</table>

## Effect upon regulation voltage

<table>
<thead>
<tr>
<th></th>
<th>CCM 120-3</th>
<th>CCM 120-4</th>
<th>CC 116-2</th>
<th>CC 117-2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>91</td>
<td>91</td>
<td>108</td>
<td>114</td>
</tr>
<tr>
<td></td>
<td>89</td>
<td>92</td>
<td>93</td>
<td>91</td>
</tr>
<tr>
<td></td>
<td>87</td>
<td></td>
<td>92</td>
<td>90</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>89</td>
<td>89</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Time (minutes)</th>
<th>BD</th>
<th>V10 m.a.</th>
<th>V50 m.a.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>116</td>
<td>89</td>
<td>94</td>
</tr>
<tr>
<td>5</td>
<td>119</td>
<td>96</td>
<td>101</td>
</tr>
<tr>
<td>10</td>
<td>122</td>
<td>103</td>
<td>108</td>
</tr>
<tr>
<td>15</td>
<td>131</td>
<td>104</td>
<td>113</td>
</tr>
<tr>
<td>20</td>
<td>130</td>
<td>110</td>
<td>118</td>
</tr>
<tr>
<td>25</td>
<td>138</td>
<td>109</td>
<td>116</td>
</tr>
</tbody>
</table>

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:

<table>
<thead>
<tr>
<th>Half clear bulb</th>
<th>147-6</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>51</td>
<td>47.5</td>
<td>37</td>
</tr>
<tr>
<td>Very Opaque bulb</td>
<td>40</td>
<td>46</td>
<td></td>
<td>37</td>
</tr>
</tbody>
</table>

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 vapor 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

\[
\begin{align*}
2 \text{CsCl} &= 2 \text{Cs} + \text{Cl}_2 \\
\text{Ca} + \text{Cl}_2 &= \text{CaCl}_2 \\
\text{Ca} + 2 \text{CsCl} &= \text{CaCl}_2 + 2 \text{Cs} \\
\end{align*}
\]

\[\Delta H = +212,800 \text{ cal.} \]

\[\Delta H = -190,300 \text{ cal.} \]

\[\Delta H = +22,500 \text{ cal.} \]

Results for the other alkalis give

\[
\begin{align*}
\text{Ca} + 2 \text{KCl} &= \text{CaCl}_2 + 2 \text{K} \\
\text{Ca} + 2 \text{NaCl} &= \text{CaCl}_2 + 2 \text{Na} \\
\text{Ca} + 2 \text{RbCl} &= \text{CaCl}_2 + 2 \text{Rb} \\
\end{align*}
\]

\[\Delta H = +3,780 \text{ cal.} \]

\[\Delta H = +5,100 \text{ cal.} \]

\[\Delta H = +19,700 \text{ cal.} \]

Now at room temperature \[\Delta C_p\] for the caesium reaction is

\[\Delta C_p = C_{\text{CaCl}_2} + 2 C_{\text{Cs}} - C_{\text{CsCl}} - 2 C_{\text{CsCl}}
\]

\[= 18.2 + 16.0 - 7.0 - 25.2 = 2.2 \text{ cal.} \]

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 these are rather complete data for these reactions in melts over lead. Jellinek and Czerwinski 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

$$2\text{Na} + \text{CaCl}_2 \rightarrow 2\text{NaCl} + \text{Ca}$$

has a constant

$$\left(\frac{100-y}{y}\right) \left(\frac{x}{100-x}\right) = K = .21$$

where $x = \text{mol percentage of } \text{CaCl}_2$ and

$y = \text{atom percentage of Ca}$

They found a changing order of the alkalis in the electromotive 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.

<table>
<thead>
<tr>
<th>Substance</th>
<th>Melting point</th>
<th>Boiling point</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cs</td>
<td>28.5</td>
<td>670</td>
</tr>
<tr>
<td>K</td>
<td>62.5</td>
<td>912</td>
</tr>
<tr>
<td>Rb</td>
<td>39</td>
<td>676</td>
</tr>
<tr>
<td>Na</td>
<td>97.9</td>
<td>750</td>
</tr>
<tr>
<td>Li</td>
<td>179</td>
<td>1400</td>
</tr>
<tr>
<td>Ca</td>
<td>785</td>
<td></td>
</tr>
<tr>
<td>CaCl₂</td>
<td>780</td>
<td>900 probably</td>
</tr>
<tr>
<td>CsCl</td>
<td>645</td>
<td>1303</td>
</tr>
<tr>
<td>RbCl</td>
<td>715</td>
<td>1410</td>
</tr>
<tr>
<td>KCl</td>
<td>775</td>
<td>1447</td>
</tr>
<tr>
<td>NaCl</td>
<td>800</td>
<td>1439</td>
</tr>
<tr>
<td>LiCl</td>
<td>614</td>
<td>1360</td>
</tr>
</tbody>
</table>
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 on caesium was supplemented by that of Killian on rubidium; and collected data of Landolt-Bornstein on sodium supply the essential alkali data. There are no data on lithium. Calcium data have lately been critically revised by Dr. Jones, and the data on chlorides are derived from Walker and from my computation from Landolt-Bornstein.

\[
\log_{10} \frac{p}{p_{\text{bs}}} = \frac{A}{T} - B
\]

The ratio \(p_{\text{cs}}/p_{\text{ca}}\) is given by

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

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 well neglect 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

\[
\Delta F = -RT\ln K_p = -2 RT\ln p_{\text{cs}}
\]

Then considering the vacuum under which we work to be 1 bar,
<table>
<thead>
<tr>
<th>Substance</th>
<th>A</th>
<th>B</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cs</td>
<td>10.65</td>
<td>3992</td>
<td>10</td>
</tr>
<tr>
<td>Rb</td>
<td>10.55</td>
<td>4132</td>
<td>&quot;</td>
</tr>
<tr>
<td>K</td>
<td>11.83</td>
<td>4964</td>
<td>&quot;</td>
</tr>
<tr>
<td>Na</td>
<td>9.86</td>
<td>4875</td>
<td>&quot;</td>
</tr>
<tr>
<td>Ca</td>
<td>15.0</td>
<td>12750</td>
<td>Own calculation</td>
</tr>
<tr>
<td>CsCl</td>
<td>11.19</td>
<td>8170</td>
<td>Jones-Lewis</td>
</tr>
<tr>
<td>RbCl</td>
<td>10.998</td>
<td>8260</td>
<td>13</td>
</tr>
<tr>
<td>KCl</td>
<td>11.53</td>
<td>9150</td>
<td>&quot;</td>
</tr>
<tr>
<td>NaCl</td>
<td>11.22</td>
<td>9260</td>
<td>&quot;</td>
</tr>
<tr>
<td>LiCl</td>
<td>10.92</td>
<td>8130</td>
<td>13</td>
</tr>
</tbody>
</table>
This reaction would run to \( \ln p_{\text{Cs}} = 0 \) if \( 10.65 - 3992/T \).

This is at a temperature of \( 375^\circ \text{K} \). At this temperature, the rate of evaporation of Cs would be:

\[ 43.74 \times 10^{-6} \left( \frac{132.8 \times 1}{375} \right) \]

\[ 26. \times 10^{-6} \text{ gms/sec. cm}^2 \]

Now no Cs is produced during long (15-30 min.) bakeout at temperatures as high as \( 600^\circ \text{K} \) where both equilibrium, diffusion, 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 solid solid Ca, although at the higher temperatures (in the reaction, for instance) the liquid must be fairly homogeneous with molten Ca.

Let us consider the energy relations in the typical reaction

\[ \text{Ca} + 2 \text{NaCl} \rightarrow \text{CaCl}_2 + 2 \text{Na} \]

Since data are rather complete for it.

\[ \Delta H_{298} = 5100 \text{ cal. (solids)} \]

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

Estimating \( S_{298} \) for CaCl\(_2\) by Latimer's rule:

\[ S_{\text{CaCl}_2} = \frac{3}{2} R \ln 40.07 - .94 = 10.64 \]

\[ \frac{+2 \times \frac{3}{2} R \ln 35.46 - .94=9.32}{=29.96} \]

\[ 2 S_{\text{Na (solid)}} = 24.4 \quad S_{\text{Ca}} = 10.64 \]

\[ S_{\text{CaCl}_2} = \frac{29.96}{54.36} \quad 2 S_{\text{NaCl}} = \frac{34.8}{45.44} \]
19.

(S NaCl is from p. 2573, Vol. 39, J.A.C.S., Lewis and Gibson)

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

Now \( \Delta F \) for the process \( 2 \text{Na}_s \rightarrow 2 \text{Na}_g \)
\( = -2\text{RT} \ln \frac{10^{-12.49}}{1} = 2(-592 \times 2.303 \times -12.49) \)
\( = 2(17050) \text{ cal.} \)
\( = 34100 \text{ cal.} \)

Hence for the reaction

\( \text{Ca}_s + 2 \text{NaCl} \rightarrow \text{CaCl}_2 + 2 \text{Na}_g \)

\( \Delta F \) is 2440 + 34,100 = 36540 cal.

For this last process

\( \Delta S = (70.12 + 29.96) - (10.64 + 34.3) = 54.64 \)
\( \Delta H = \Delta F + T \Delta S = 25400 + 54.64 \times 238 = 52820 \text{ cal.} \)

Now \( \Delta H = \Delta H_0 + \Delta C_p \times T \)

\( C_p \text{Ca} = 6.4 + 0.001 T \) for range

\( C_p \text{2NaCl} = 25.6 \)
\( C_p \text{CaCl}_2 = 18.22 \)
\( C_p \text{2Na} = 10 \)

Hence \( \Delta C_p = 28.22 - (32.0 + 0.001 T) = -3.78 - 0.001T \)
\( \Delta H_0 = 52820 + 3.78 \times T + 0.001 \times T^2 \)
\( = 52820 + 1125 \times 90 = 54035 \)
\( \Delta F = 54035 + 3.78 \times T \ln T + 0.0005 \times T^2 + 1 \times T \)
\( I = \frac{36540 - 54035 - 6400 - 45}{198} = -23940 \)

or I = -80.5
A similar calculation gives for

\[
\text{Ca}_2 + 2 \text{CsCl} = \text{CaCl}_2 + 2 \text{Cs}_2
\]

\[
\Delta H_{298} = 43,350
\]

\[
\Delta F_{298} = 23,150
\]

\[
\Delta H = 44,470 - 3.48 T - 0.001 T^2
\]

\[
\Delta F = 44,470 + 3.48 T \ln T + 0.0005 T^2 - 91.6 T
\]

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°C. At 600°C the lowest temperature for production of Cs, \( p_{\text{Cs}} = 10^4 \) bars, \( p_{\text{Ca}} = 10^{-6} \) bars.

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

The compounds \( \text{CaCl}_2 - \text{LiCl} \) (492°C), \( \text{CaCl}_2 - 4 \text{NaCl} \) (580°C), \( \text{CaCl}_2 - \text{KCl} \) (754°C) 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°C 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. (cm²). The whole yield of caesium may be seen to condense practically instantaneously after the first deposit on the walls.
Langmuir's formula gives:

\[
m(\text{gms per sec}) = 43.74 \times 10^{-6} \sqrt{\frac{M}{T}} p(\text{bars})
\]

\[
= 43.74 \times 10^{-6} \sqrt{\frac{M}{T}} 10 A - B
\]

<table>
<thead>
<tr>
<th>Substance</th>
<th>M</th>
<th>((43.74 \times 10^{-6} \sqrt{M}))</th>
<th>(m(900^\circ\text{K}))</th>
<th>(p(900^\circ\text{K}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cs</td>
<td>132.8</td>
<td>504 x (10^{-6})</td>
<td>27.7 gm.</td>
<td>1.65 (\times 10^{-6}) bars</td>
</tr>
<tr>
<td>Rb</td>
<td>85.5</td>
<td>404 &quot;</td>
<td>12.25 &quot;</td>
<td>30 &quot; &quot;</td>
</tr>
<tr>
<td>K</td>
<td>39.1</td>
<td>273</td>
<td>18.9 &quot;</td>
<td>2.09 &quot; &quot;</td>
</tr>
<tr>
<td>Na</td>
<td>23.0</td>
<td>210</td>
<td>.194</td>
<td>.28 &quot; &quot;</td>
</tr>
<tr>
<td>Li</td>
<td>6.94</td>
<td>115</td>
<td>.00526</td>
<td>.00085 &quot; &quot;</td>
</tr>
</tbody>
</table>

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

\[
\text{Cs}_2\text{CO}_3 + \text{Ca} \rightarrow \text{CaO} + \text{CO}_2 + 2\text{Cs}
\]

will very possibly remove the \(\text{CO}_2\) 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 temperature coefficient of diffusion; particularly in the liquid reaction $\text{Ca}_s + 2 \text{CsCl}_l \rightarrow \text{CaCl}_2_s + 2 \text{Cs}_g$

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

Alloying: Mellor states that little alloying takes place between the alkali 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. 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.

Thermal conductivity of He = \(0.34 \times 10^{-3} \text{ cm·cal/cm·sec·°C}\).

" " " \(Ne = 0.12 \times 10^{-3}\) "

" " " of a mixture \(\frac{75\text{ Ne}}{25\text{ He}} = 0.18 \times 10^{-3}\) "

\[Wc = \frac{2\pi H l \Delta T}{\log \left( \frac{r_0}{r} \right) + f \left( \frac{t}{r} - \frac{t}{r_0} \right)}\]

Now the Smoluchowski formula for such a case in a gas at low pressure gives.
when

\[ H = \text{thermal conductivity} \]
\[ \ell = \text{length of cylinder} \]
\[ r_0 = \text{radius of glass wall} \]
\[ r_1 = \text{radius of cylinder} \]
\[ \gamma = \text{a function of the mean free path which in this case is comparable to hydrogen for which } \gamma = 0.008 \]

Then

\[ \Delta T = \frac{4.5}{2 \times 6.28 \times 0.18 \times 10^{-3} \times 5 \times 0.69 + 0.008 \left( \frac{1}{1.25} - \frac{1}{2.5} \right)} = 270^\circ C. \]

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

\[ W_{\text{leads}} = 2 \times \left( \frac{1.142 \times (270 + 25) \times 0.58}{7.5} \right) = 2 \times 2 = 4.5 \text{ watts} \]

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

\[ \Delta T_{\text{glass}} = \frac{4.0}{1.25 \times 0.0015} = 2.1^\circ C. \]

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. Kingdom 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 sufficient to clean up externally large amounts of reactive gases - as for instance 20 cc of oxygen at atmospheric pressure (≈.002 9\text{ton} 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 doubt 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 characteristics approaching nearer Cs than Rb, correlates with the anomalous behavior at high pressures found by Bridgman.20

The reactions typified by

\[ 2 \text{CsCl} + \text{Cs} \rightarrow \text{CsCl}_2 + 2 \text{Cs} \]

have been studied for equilibrium and kinetics.

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

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

2. Extension of the method used in studying reaction of formation by more exact measurements.

3. Extension of thermodynamic theory to the cathode phenomena.
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System for evacuation and gas filling of alkali metal–rare gas glow tubes.

GENERAL ELECTRIC COMPANY.
Fig. 3.

Tube and thermocouple arrangement.
Ageing Characteristics
(average)

Breakdown Voltage

Ageing hours
Equilibrium Electrical Characteristics

Watts and \( \sqrt{\text{Estimated Cathode Temperature}} \)

Dotted line = instantaneous characteristics

Estimated Cathode Temperature

\[ 10 \quad 20 \quad 25 \quad 30 \]
Fig. 5

Electrical Characteristics vs Ambient Temperature

Ambient Temperature °C

Voltage

Breakdown

Regulation
Fig. 6.

Vapour Pressures of the Alkali Metals

$\log_{10} p \text{ (bars)} \text{ vs. } \frac{1}{T \times \text{R}}$

$log_{10} p \text{ (bars)}$

$\frac{1}{T \times \text{R}}$

10 hours
Vapor Pressure
of
Hg, Cs, Rb, K, and Na.
Payne
11/0/21.