Alkali Metal Vapor Pressures & Number Densities for Hybrid Spin Exchange Optical Pumping

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Abstract

Vapor pressure curves and number density formulas for the alkali metals are listed and compared from the 1995 CRC, Nesmeyanov, and Killian. Formulas to obtain the temperature, the dimer to monomer density ratio, and the pure vapor ratio given an alkali density are derived. Considerations and formulas for making a prescribed hybrid vapor ratio of alkali to Rb at a prescribed alkali density are presented.

Contents

1 Vapor Pressure Curves

1.1 The Clausius-Clapeyron Equation

The saturated vapor pressure above a liquid (solid) is described by the Clausius-Clapeyron equation. It is a consequence of the equality between the chemical potentials of the vapor and liquid (solid). The derivation can be found in any undergraduate text on thermodynamics (e.g. Kittel & Kroemer [1]):

$$\Delta v \cdot \partial P = L \cdot \partial T / T \tag{1}$$

where P is the pressure, T is the temperature, L is the latent heat of vaporization (sublimation) per particle, and Δv is given by:

$$\Delta v = v_{\mathtt{v}} - v_{\mathtt{l(s)}} = \frac{V_{\mathtt{v}}}{N_{\mathtt{v}}} - \frac{V_{\mathtt{l(s)}}}{N_{\mathtt{l(s)}}} \tag{2}$$

where V is the volume occupied by the particles, N is the number of particles, and the subscripts v & l(s) refer to the vapor & liquid (solid) respectively.

Following the derivation in Nesmeyanov [2], we'll make the approximation that the average volume per vapor atom is much greater than the average volume per liquid (solid) atom:

$$v_{\mathtt{v}} \gg v_{\mathtt{l(s)}} \qquad \Rightarrow \qquad \Delta v \approx v_{\mathtt{v}} = \frac{V_{\mathtt{v}}}{N_{\mathtt{v}}} \tag{3}$$

Since the vapor has a very low density, we can apply the ideal gas law:

$$PV_{\mathtt{v}} = N_{\mathtt{v}} kT \tag{4}$$

to get:

$$(kT/P) \cdot \partial P = L \cdot \partial T / T \tag{5}$$

where $k = 1.3806504{\times}10^{-23}\ \mathrm{Pa \cdot m^3/K}$ is Boltzmann's constant. Expanding the latent heat as a function of temperature,

$$L(T) = L_0 + L_1 T + L_2 T^2 + \cdots \tag{6}$$

and a little rearrangement gives:

$$\frac{\partial P}{P} = \left(\frac{L_0}{kT^2} + \frac{L_1}{kT} + \frac{L_2}{k} + \cdots \right) \partial T \tag{7}$$

Integrating the above equation term by term and making substitutions for the coefficients gives the vapor pressure curve:

$$\log P_{\mathtt{vp}} = A - \frac{B}{T} + CT + D \log T \tag{8}$$

Note that the coefficients A, B, C, & D depend on whether a liquid or solid is being considered, the choice of units for the vapor pressure $P_{\mathtt{vp}}$, and the base for the logarithm. The temperature T, however, is always in Kelvin.

1.2 Number Density Formulas

The number density is obtained from the vapor pressure curve by once again applying the ideal gas law:

$$[\mathrm{A}] = \frac{N_{\mathtt{v}}}{V_{\mathtt{v}}} = \frac{P_{\mathtt{vp}}}{kT} \tag{9}$$

For all alkali metals, the number density (in units of $1/\mathrm{cm}^3$) from the 1995 CRC [4] can be written in the following equivalent forms:

$$\begin{aligned} [\mathrm{A}] &= \left[\left(\frac{101325\ \mathrm{Pa}}{1\ \mathrm{atm}} \right) \left(10^{A-B/T}\ \mathrm{atm} \right) \right] \cdot \left[\frac{1}{kT} \left(\frac{1\ \mathrm{m}}{100\ \mathrm{cm}} \right)^3 \right] && (10) \\ &= [\mathrm{A}]_0 \left(\frac{T_0}{T} \right) \exp\left(b \left[1 - \frac{T_0}{T} \right] \right) && (11) \end{aligned}$$

where A & B are parameters from the CRC and $[\mathrm{A}]_0$, T_0, & b are parameters derived from them. These parameters are different for the vapor pressure above liquid and solid. At the melting point, the liquid and solid CRC formulas give values that are consistent within the quoted accuracy, see Tab. (2). Note that T_0 is the temperature corresponding to a density of $[\mathrm{A}]_0$.

The inversion formula used to obtain the temperature given the number density is of the form:

$$T = \frac{T_0}{1 - \sum_{n=1}^{N} a_n \cdot (\ \log [\mathrm{A}]/[\mathrm{A}]_0\ )^n} \tag{12}$$

The coefficients $\{a_n\}$ are found from a fit to the Eqn. (12). The value of highest order N is found by keeping the temperature residuals under 0.02 K (0.005K) for liquids (solids) over the temperature range noted in the CRC. If only the lowest order term is kept ($N = 1$), then we get the following formula that is good to ± 2.5 K for Li and ± 1.2 K for all others:

$$T = \frac{T_0}{1 - a_1 \cdot \log [\mathrm{A}]/[\mathrm{A}]_0} \tag{13}$$

The values for parameters A, B, T_0, $[\mathrm{A}]_0$, b, & $\{a_n\}$ are listed in Tab. (1).

1.3 Comparison with other standard formulas

The Nesmeyanov [2] formula for the alkali number density (in 1/cm^3) is written as:

$$[\mathrm{A}] = \left[\left(\frac{101325 \text{ Pa}}{760 \text{ mmHg}} \right) \left(10^{A - B/T + CT + D \log_{10} T} \text{ mmHg} \right) \right] \cdot \left[\frac{1}{kT} \left(\frac{1 \text{ m}}{100 \text{ cm}} \right)^3 \right] \tag{14}$$

There are no uncertainties quoted. Nesmeyanov does not list values for the K vapor pressure above a solid; therefore, we'll extrapolate to lower temperatures using the liquid values.

Killian [5] made measurements of K and Rb and fit them to:

$$[\mathrm{A}] = \left[\left(\frac{1 \text{ Pa}}{10 \text{ barye}} \right) \left(10^{A - B/T} \text{ barye} \right) \right] \cdot \left[\frac{1}{kT} \left(\frac{1 \text{ m}}{100 \text{ cm}} \right)^3 \right] \tag{15}$$

There were no uncertainties quoted. In addition, Killian quotes the pressure in "bars." His formula is incorrect by 6 orders of magnitude if one interprets his "bar" as 10^5 Pascals. However, it has been noted [6] that there exists another pressure unit "barye," which is equivalent to 0.1 Pascals. We'll assume that "barye" is the unit meant by Killian.

The parameters A, B, C, & D for Nesmeyanov & Killian are listed in Tab. (3). Fig. (1) shows both the vapor pressures and number densities from all three sources; whereas Fig. (2) depicts the percent difference between Nesmeyanov & Killian relative to the CRC. Nesmeyanov appears to be systematically 10% to 30% lower. The Killian values for Rb compare favorably to the CRC and are about 10% lower over the temperature range covered by Killian's measurements. Outside that range, the Killian values are within -10% and $+20\%$ of the CRC values. Within the measurement range, the Killian K values compare favorably to the CRC, but outside that range, the Killian values diverge from the CRC significantly.

1.4 Alkali Dimers

Dimers are weakly bound molecules formed by two alkali atoms. Only Nesmeyanov [2] includes a formula for alkali dimers in vapor form:

$$[\mathrm{A}_2] = \left[\left(\frac{101325 \text{ Pa}}{760 \text{ mmHg}} \right) \left(10^{A - B/T + CT + D \log_{10} T} \text{ mmHg} \right) \right] \cdot \left[\frac{1}{kT} \left(\frac{1 \text{ m}}{100 \text{ cm}} \right)^3 \right] \tag{16}$$

No uncertainties are quoted. The Cs liquid and solid dimer number densities have a large discrepancy at the melting point. Therefore, we'll use the liquid vapor pressure to extrapolate down to lower temperatures for Cs.

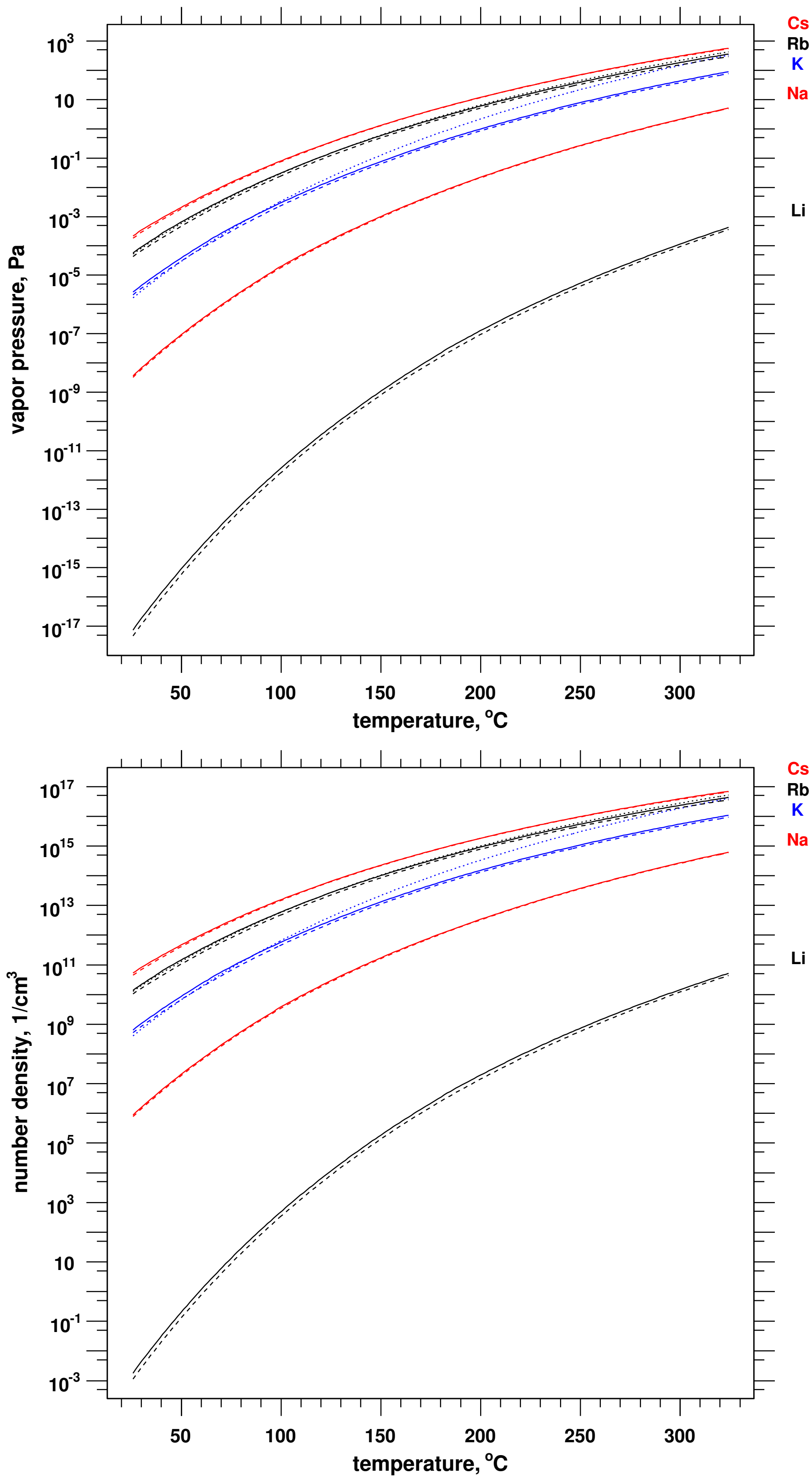

Figure 1: Number Density and Vapor Pressure Curves. The solid lines represent the CRC formula [4]. The dashed lines represent the Nesmeyanov formula [2]. The dotted lines represent Killian [5].

<table>
<tr><th colspan="6">CRC</th></tr>
<tr><th>over solid</th><th>Li</th><th>Na</th><th>K</th><th>Rb</th><th>Cs</th></tr>
<tr><td>$T_{\mathtt{min}}$ (K)</td><td colspan="5">298</td></tr>
<tr><td>$T_{\mathtt{min}}$ (°C)</td><td colspan="5">25</td></tr>
<tr><td>$[\mathrm{A}]_{\mathtt{min}}$ (1/cm^3)</td><td>1.49×10^{-3}</td><td>7.72×10^{5}</td><td>5.78×10^{8}</td><td>1.27×10^{10}</td><td>4.82×10^{10}</td></tr>
<tr><td>$T_{\mathtt{mp}}$ (K)</td><td>453.7</td><td>370.87</td><td>336.53</td><td>312.46</td><td>301.59</td></tr>
<tr><td>$T_{\mathtt{mp}}$ (°C)</td><td>180.5</td><td>97.72</td><td>63.38</td><td>39.31</td><td>28.44</td></tr>
<tr><td>$[\mathrm{A}]_{\mathtt{mp}}$ (1/cm^3)</td><td>3.61×10^{6}</td><td>3.07×10^{9}</td><td>3.12×10^{10}</td><td>5.47×10^{10}</td><td>6.88×10^{10}</td></tr>
<tr><td>A</td><td>5.667</td><td>5.298</td><td>4.961</td><td>4.857</td><td>4.711</td></tr>
<tr><td>B (K)</td><td>8310</td><td>5603</td><td>4646</td><td>4215</td><td>3999</td></tr>
<tr><td>T_0 (K)</td><td>378.51</td><td>336.79</td><td>302.76</td><td>295.75</td><td>283.12</td></tr>
<tr><td>$[\mathrm{A}]_0$ (1/cm^3)</td><td>10^{3}</td><td>10^{8}</td><td>10^{9}</td><td>10^{10}</td><td>10^{10}</td></tr>
<tr><td>b</td><td>50.552</td><td>38.306</td><td>35.334</td><td>32.816</td><td>32.523</td></tr>
<tr><td>$a_1 \times 10^2$</td><td>2.0181</td><td>2.6806</td><td>2.9125</td><td>3.1447</td><td>3.1752</td></tr>
<tr><td>$a_2 \times 10^5$</td><td>0.41582</td><td>0.94564</td><td>1.3149</td><td colspan="2">0</td></tr>
<tr><td>$a_3 \times 10^8$</td><td>5.2686</td><td colspan="4">0</td></tr>
<tr><td>a_4</td><td colspan="5">0</td></tr>
<tr><th>over liquid</th><th>Li</th><th>Na</th><th>K</th><th>Rb</th><th>Cs</th></tr>
<tr><td>$T_{\mathtt{mp}}$ (K)</td><td>453.7</td><td>370.87</td><td>336.53</td><td>312.46</td><td>301.59</td></tr>
<tr><td>$T_{\mathtt{mp}}$ (°C)</td><td>180.5</td><td>97.72</td><td>63.38</td><td>39.31</td><td>28.44</td></tr>
<tr><td>$[\mathrm{A}]_{\mathtt{mp}}$ (1/cm^3)</td><td>3.79×10^{6}</td><td>3.18×10^{9}</td><td>3.22×10^{10}</td><td>5.66×10^{10}</td><td>7.11×10^{10}</td></tr>
<tr><td>$T_{\mathtt{max}}$ (K)</td><td>1000</td><td>700</td><td>600</td><td colspan="2">550</td></tr>
<tr><td>$T_{\mathtt{max}}$ (°C)</td><td>727</td><td>427</td><td>327</td><td colspan="2">277</td></tr>
<tr><td>$[\mathrm{A}]_{\mathtt{max}}$ (1/cm^3)</td><td>7.90×10^{15}</td><td>1.10×10^{16}</td><td>1.17×10^{16}</td><td>1.24×10^{16}</td><td>2.12×10^{16}</td></tr>
<tr><td>A</td><td>5.055</td><td>4.704</td><td>4.402</td><td>4.312</td><td>4.165</td></tr>
<tr><td>B (K)</td><td>8023</td><td>5377</td><td>4453</td><td>4040</td><td>3830</td></tr>
<tr><td>T_0 (K)</td><td>800.94</td><td>546.90</td><td>463.79</td><td>422.98</td><td>406.51</td></tr>
<tr><td>$[\mathrm{A}]_0$ (1/cm^3)</td><td colspan="5">10^{14}</td></tr>
<tr><td>b</td><td>23.065</td><td>22.638</td><td>22.108</td><td>21.993</td><td>21.694</td></tr>
<tr><td>$a_1 \times 10^2$</td><td>4.5321</td><td>4.6214</td><td>4.7377</td><td>4.7636</td><td>4.8324</td></tr>
<tr><td>$a_2 \times 10^5$</td><td>4.6950</td><td>4.9639</td><td>5.4499</td><td>5.5431</td><td>5.8187</td></tr>
<tr><td>$a_3 \times 10^6$</td><td>1.4241</td><td>1.6648</td><td>1.6322</td><td>1.7177</td><td>1.9172</td></tr>
<tr><td>$a_4 \times 10^8$</td><td>2.8057</td><td>4.5433</td><td colspan="3">0</td></tr>
</table>

Table 1: CRC Number Density Parameters. The parameters listed are used in Eqns. (10), (11), (12), & (13). The CRC [4] vapor pressure formulas have a quoted accuracy of 5%. The inversion formula for the temperature reproduces the CRC values to within ±0.02 K (±0.005 K) given the vapor pressure above a liquid (solid). If only the lowest order term is used (a_1), then the inversion formula reproduces the CRC values to ±2.5 K for Li and ±1.2 K for all others. The fit to Li is worse because it the data covers a much large number density range.

	Melting		CRC		% diff.	avg.
	°C	K	over solid	over liquid		
Li	180.5	453.65	3.61×10^6	3.79×10^6	4.8	3.70×10^6
Na	97.72	370.87	3.07×10^9	3.18×10^9	3.6	3.12×10^9
K	63.38	336.53	3.12×10^{10}	3.22×10^{10}	3.4	3.17×10^{10}
Rb	39.31	312.46	5.47×10^{10}	5.66×10^{10}	3.5	5.57×10^{10}
Cs	28.44	301.59	6.88×10^{10}	7.11×10^{10}	3.3	6.99×10^{10}

Table 2: CRC Number Density at the Melting Point. The CRC solid and liquid vapor pressure curves give two different values at the melting point. However, the difference is always less than 5%, which is the quoted accuracy for the CRC formula.

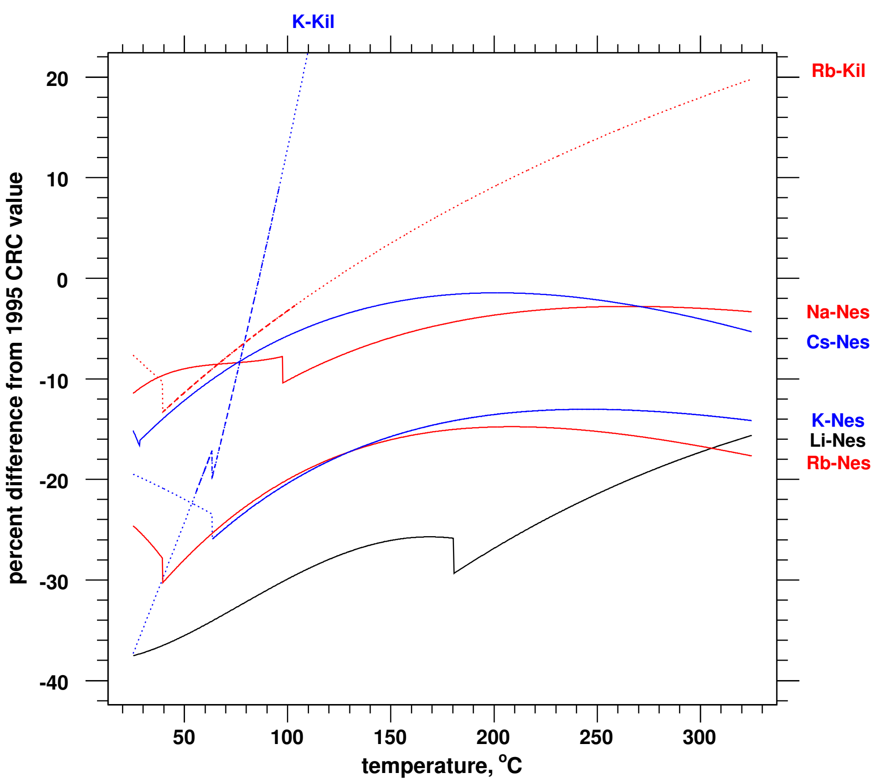

Figure 2: Relative Difference Between Formulas. The solid lines represent the % difference between Nesmeyanov and the CRC. The dashed lines represent the % difference between Killian and the CRC over the temperature range measured in Killian. The dotted lines represent extrapolations outside the temperature ranges quoted for the formulas. The discontinuities are mainly attributable to the CRC formulas and occur only at the melting point.

Nesmeyanov					
over solid	**Li**	**Na**		**Rb**	**Cs**
$T_{\mathtt{min}}$ (K)			298		
$T_{\mathtt{min}}$ (°C)			25		
$[\mathrm{A}]_{\mathtt{min}}$ (1/cm^3)	9.29×10^{-4}	6.83×10^{5}		9.59×10^{9}	4.10×10^{10}
$T_{\mathtt{mp}}$ (K)	453.7	370.87		312.46	301.59
$T_{\mathtt{mp}}$ (°C)	180.5	97.72		39.31	28.44
$[\mathrm{A}]_{\mathtt{mp}}$ (1/cm^3)	2.68×10^{6}	2.83×10^{9}		3.95×10^{10}	5.72×10^{10}
$-A$	54.87864	-133.42927		94.04826	219.48200
B (K)	6450.944	9302.868		1961.258	-1088.676
$-C$ (1/K) $\times 10^2$	1.487480	-3.114431		3.771687	8.336185
D	24.82251	-49.37679		42.57526	94.88752
over liquid	**Li**	**Na**	**K**	**Rb**	**Cs**
$T_{\mathtt{mp}}$ (K)	453.7	370.87	336.53	312.46	301.59
$T_{\mathtt{mp}}$ (°C)	180.5	97.72	63.38	39.31	28.44
$[\mathrm{A}]_{\mathtt{mp}}$ (1/cm^3)	2.68×10^{6}	2.85×10^{9}	2.39×10^{10}	3.95×10^{10}	5.96×10^{10}
$T_{\mathtt{bp}}$ (K)	1615	1156	1032	961	944
$T_{\mathtt{bp}}$ (°C)	1342	883	759	688	671
$[\mathrm{A}]_{\mathtt{bp}}$ (1/cm^3)	4.23×10^{18}	5.50×10^{18}	6.08×10^{18}	6.49×10^{18}	6.85×10^{18}
A	10.34540	10.86423	13.83624	15.88253	8.22127
B (K)	8345.574	5619.406	4857.902	4529.635	4006.048
C (1/K) $\times 10^4$	-0.8840	0.0345	3.4940	5.8663	-6.0194
$-D$	0.68106	1.0411	2.21542	2.99138	0.19623

Killian		
	K	**Rb**
$T_{\mathtt{min}}$ (K)	328.8	312.5
$T_{\mathtt{min}}$ (°C)	55.6	39.4
$[\mathrm{A}]_{\mathtt{mp}}$ (1/cm^3)	1.19×10^{10}	4.93×10^{10}
$T_{\mathtt{max}}$ (K)	369.2	376.8
$T_{\mathtt{max}}$ (°C)	96.1	103.6
$[\mathrm{A}]_{\mathtt{max}}$ (1/cm^3)	4.76×10^{11}	7.38×10^{12}
A	11.83	10.55
B (K)	4964	4132

Table 3: Alternative Number Density Parameters. The Nesmeyanov [2] parameters are used in Eqn. (14) and the Killian [5] parameters are using in Eqn. (15).

Nesmeyanov Dimer to Monomer Ratio					
	Li	**Na**	**K**	**Rb**	**Cs**
$T_{\mathtt{min}}$ (K)	453.65	370.87	336.53	312.46	301.59
$T_{\mathtt{min}}$ (°C)	180.5	97.72	63.38	39.31	28.44
$[\mathrm{A}]_{\mathtt{min}}$ (1/cm^3)	2.68×10^{6}	2.85×10^{9}	2.39×10^{10}	3.95×10^{10}	5.96×10^{10}
$([\mathrm{A}_2]/[\mathrm{A}])_{\mathtt{min}}$	5.93×10^{-5}	3.48×10^{-4}	2.49×10^{-5}	3.48×10^{-5}	2.09×10^{-5}
$T_{\mathtt{max}}$ (K)	1050	700	600	550	
$T_{\mathtt{max}}$ (°C)	777	427	327	277	
$[\mathrm{A}]_{\mathtt{max}}$ (1/cm^3)	1.62×10^{16}	1.04×10^{16}	1.00×10^{16}	1.04×10^{16}	2.06×10^{16}
$([\mathrm{A}_2]/[\mathrm{A}])_{\mathtt{max}}$	0.0357	0.0253	4.85×10^{-3}	5.39×10^{-3}	5.24×10^{-3}
$[\mathrm{A}]_0$ (1/cm^3)			10^{14}		
$([\mathrm{A}]/[\mathrm{A}_2])_0$	119	148	1350	1210	1920
n	0.284	0.284	0.407	0.404	0.433

Table 4: Dimer to Monomer Ratio vs. Monomer Density. This parameters are used in Eqn. (18). The temperature range of the fit covers the higher melting point to a temperature that corresponds to monomer density of at least 10^{16} 1/cm^3. These parameters reproduce the Nesmeyanov [2] values to within ±10%.

The ratio of the Nesmeyanov dimer to monomer density (or vapor pressure) is fit to the following two forms:

$$\frac{[\mathrm{A}_2]}{[\mathrm{A}]} = \frac{\exp\left(-b\left(\frac{T_0}{T}-1\right)+c\left(\frac{T}{T_0}-1\right)+d\cdot\log\left(\frac{T}{T_0}\right)\right)}{([\mathrm{A}]/[\mathrm{A}_2])_0} \tag{17}$$

$$= \frac{([\mathrm{A}]/[\mathrm{A}]_0)^n}{([\mathrm{A}]/[\mathrm{A}_2])_0} \tag{18}$$

The first form is fit to values over a temperature range that covers 298 K to 600 K. Even though this range covers the discontinuity at the melting point, the fit still reproduces the Nesmeyanov values to within ±5%. The second form is fit to values over a temperture range that runs from the melting point to a temperature that corresponds to at least 10^{16}. Because of the larger range covered, it only reproduces the Nesmeyanov values to ±10%. Note that the ratio $([\mathrm{A}]/[\mathrm{A}_2])_0$ corresponds to a temperature T_0 for the first form and to the density $[\mathrm{A}]_0$ for the second form.

The values for the Nesmeyanov Dimer parameters A, B, C, & D for liquids and solids, as well as the parameters derived from them for the first fit formula b, c, d, T_0, & $([\mathrm{A}]/[\mathrm{A}_2])_0$ are listed in Tab. (5). The parameters for the second fit formula n, $[\mathrm{A}]_0$, & $([\mathrm{A}]/[\mathrm{A}_2])_0$ are listed in Tab. (4).

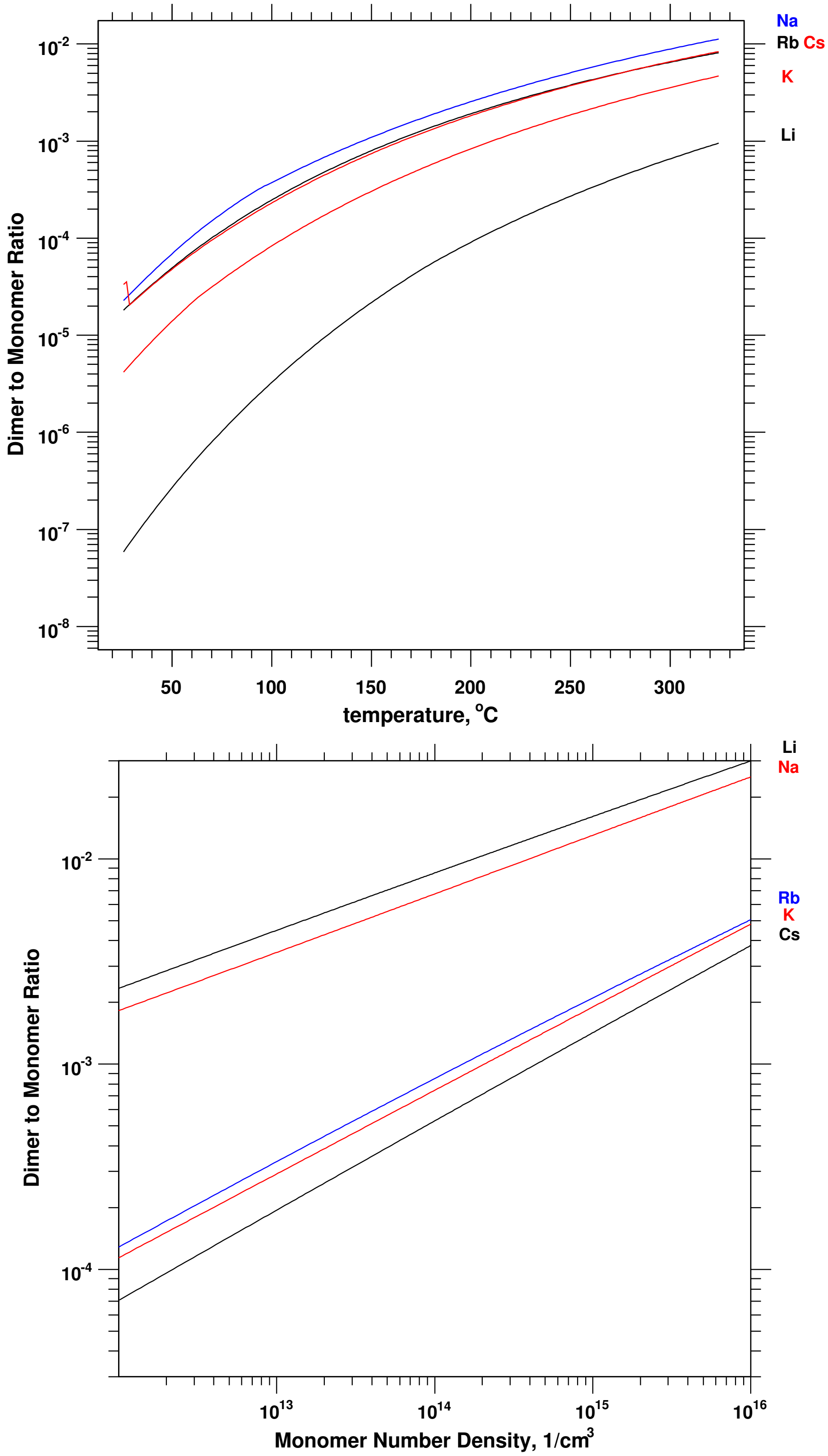

Figure 3: Dimer to Monomer Ratio vs. Temperature and Monomer Density. (Nesmeyanov [2] formulas)

Nesmeyanov Dimers					
over solid	**Li**	**Na**	**K**	**Rb**	**Cs**
$T_{\mathtt{min}}$ (K)			298		
$T_{\mathtt{min}}$ (°C)			25		
$[A_2]_{\mathtt{min}}$ (1/cm^3)	5.14×10^{-11}	14.9	1.85×10^{3}	1.67×10^{5}	1.31×10^{6}
$T_{\mathtt{mp}}$ (K)	453.7	370.87	336.53	312.46	301.59
$T_{\mathtt{mp}}$ (°C)	180.5	97.72	63.38	39.31	28.44
$[A_2]_{\mathtt{mp}}$ (1/cm^3)	148	1.01×10^{6}	5.93×10^{5}	1.27×10^{6}	2.15×10^{6}
$-A$	74.04758	338.13794	75.58292	211.33010	211.02760
B (K)	8491.378	−1842.920	4578.883	966.918	727.545
$-C$ (1/K) $\times 10^2$	2.035840	9.791968	2.667904	7.829240	7.947950
D	33.06458	139.75985	34.61890	91.59149	91.64953
over liquid	**Li**	**Na**	**K**	**Rb**	**Cs**
$T_{\mathtt{mp}}$ (K)	453.7	370.87	336.53	312.46	301.59
$T_{\mathtt{mp}}$ (°C)	180.5	97.72	63.38	39.31	28.44
$[A_2]_{\mathtt{mp}}$ (1/cm^3)	148	1.01×10^{6}	5.92×10^{5}	1.27×10^{6}	1.21×10^{6}
$T_{\mathtt{bp}}$ (K)	1615	1156	1032	961	944
$T_{\mathtt{bp}}$ (°C)	1342	883	759	688	671
$[A_2]_{\mathtt{bp}}$ (1/cm^3)	6.22×10^{17}	7.14×10^{17}	3.52×10^{17}	3.98×10^{17}	4.13×10^{17}
A	18.37849	5.33624	17.05231	41.27530	18.22054
B (K)	11139.618	6866.162	6806.144	7226.316	6064.472
C (1/K) $\times 10^3$	0.16342	−1.06668	0.12351	3.33213	0.09016
$-D$	3.03209	−1.23023	2.98966	11.85510	3.45395
$T_{\mathtt{min}}$ (K)			298		
$([A_2]/[A])_{\mathtt{min}}$	5.44×10^{-8}	2.17×10^{-5}	4.12×10^{-6}	1.72×10^{-5}	1.74×10^{-5}
$T_{\mathtt{max}}$ (K)			600		
$([A_2]/[A])_{\mathtt{max}}$	9.67×10^{-4}	1.20×10^{-2}	4.91×10^{-3}	8.32×10^{-3}	8.57×10^{-3}
T_0 (K)			500		
$([A_2]/[A])_0$	1.70×10^{-4}	3.70×10^{-3}	1.30×10^{-3}	2.82×10^{-3}	2.73×10^{-3}
b	10.939	26.735	17.484	11.862	9.019
c	−5.303	22.388	9.816	2.482	0.228
$-d$	−5.361	42.561	19.449	7.623	2.224

Table 5: Dimer Number Density Parameters. These values are from Nesmeyanov [2] and are used in Eqn. (16). The ratio Dimer to Monomer density ratio is fit to Eqn. (17) over a temperature range of 298 K to 600 K. The Cs dimer density is discontinuous at the melting point, so we use the liquid parameters even below the melting point. The K monomer number density below the melting point is estimated using the liquid parameters. The fit reproduces the Nesmeyanov values to within 5%.

2 Creating Hybrid Mixes

2.1 Predicting the hybrid vapor ratio

To estimate the vapor number density above an impure sample of an alkali metal, we use Raoult's law:

$$[\mathrm{A}] = f_{\mathtt{A}}[\mathrm{A}]_{\mathrm{pvp}} \tag{19}$$

where $[\mathrm{A}]_{\mathtt{pvp}}$ is the vapor number density above a pure sample of the alkali metal and $f_{\mathtt{A}}$ is the mole fraction of pure alkali metal within the impure mix (liquid or solid). Raoult's law is a a very good approximation because the interaction between two alkali atoms of the same species is very similar to the interaction between two alkali atoms of different species. If two alkali metals are mixed together, then the hybrid vapor ratio above the mix is simply:

$$\frac{[\mathrm{A1}]}{[\mathrm{A2}]} = \frac{f_1}{f_2} \cdot \frac{[\mathrm{A1}]_{\mathtt{pvp}}}{[\mathrm{A2}]_{\mathtt{pvp}}} \tag{20}$$

2.2 Finding the desired mole fraction

Our goal is to produce some prescribed hybrid vapor ratio of alkali to Rb, $([\mathrm{A}]/[\mathrm{Rb}])_{\mathrm{goal}}$, with some prescribed operating alkali number density, [A]. Therefore, we have to work backwards from the hybrid vapor ratio and operating alkali density to find the mole fraction ratio in the solid mix that would produce it. In principle, this is done by assuming that there are no other impurities in the alkali mix and solving the following system of equations numerically for the operating temperature $T_{\mathtt{op}}$ and the mole fraction ratio $f_{\mathtt{A}}/f_{\mathtt{Rb}}$:

$$[\mathrm{A}]_{\mathrm{goal}} = f_{\mathtt{A}}[\mathrm{A}]_{\mathtt{pvp}}(T_{\mathtt{op}}) \qquad \& \qquad \left(\frac{[\mathrm{A}]}{[\mathrm{Rb}]}\right)_{\mathrm{goal}} = \frac{f_{\mathtt{A}}}{f_{\mathtt{Rb}}} \cdot \frac{[\mathrm{A}]_{\mathtt{pvp}}(T_{\mathtt{op}})}{[\mathrm{Rb}]_{\mathtt{pvp}}(T_{\mathtt{op}})} \qquad \& \qquad f_{\mathtt{A}} + f_{\mathtt{Rb}} = 1 \tag{21}$$

where we've explicitly written out the temperature dependence of the pure vapor pressure curves.

In practice, however, we're able to derive a simple formula for the required mole fraction ratio. This is done by first finding a parameterization of the pure vapor pressure ratio as a function of the pure alkali density. Note that normally, we obtain the pure vapor pressure ratio for two alkali metals by specifying an operating temperature. Instead what we want now is to obtain the pure vapor pressure ratio by specifying the number density of a pure alkali metal corresponding to that operating temperature. This is done by fitting ratios from the CRC formula to the following functional form:

$$\left(\frac{[\mathrm{A}]}{[\mathrm{Rb}]}\right)_{\mathtt{pvp}} = \frac{\left([\mathrm{A}]_{\mathtt{pvp}}/[\mathrm{A}]_0\right)^n}{([\mathrm{Rb}]/[\mathrm{A}])_0} \tag{22}$$

where $([\mathrm{Rb}]/[\mathrm{A}])_0$ is the pure vapor pressure ratio for a density of $[\mathrm{A}]_0$ of a pure alkali metal. This is identical to the second functional form used to fit the dimer to monomer density ratio. This formula is fit to values from the CRC formula [4] over a temperature range that covers the higher melting point to a temperature that corresponds to at least 10^{16} 1/cm^3. The formula reproduces the CRC values to ±3.5% for Li and ±1.0% for all others. Tab. (6) lists the values for the fit parameters n, $([\mathrm{Rb}]/[\mathrm{A}])_0$, & $[\mathrm{A}]_0$.

Plugging this parameterization of the pure vapor pressure ratio into the hybrid vapor ratio equation, we find:

$$\left(\frac{[\mathrm{A}]}{[\mathrm{Rb}]}\right)_{\mathrm{goal}} = \frac{f_{\mathtt{A}}}{f_{\mathtt{Rb}}} \cdot \left(\frac{[\mathrm{A}]}{[\mathrm{Rb}]}\right)_{\mathtt{pvp}} = \frac{f_{\mathtt{A}}}{f_{\mathtt{Rb}}} \cdot \frac{\left([\mathrm{A}]_{\mathtt{pvp}}/[\mathrm{A}]_0\right)^n}{([\mathrm{Rb}]/[\mathrm{A}])_0} = \frac{f_{\mathtt{A}}}{f_{\mathtt{Rb}}} \cdot \frac{([\mathrm{A}]_{\mathrm{goal}}/[\mathrm{A}]_0/\mathrm{f}_{\mathtt{A}})^n}{([\mathrm{Rb}]/[\mathrm{A}])_0} \tag{23}$$

Under our conditions, the alkali metal is lighter than Rb, which implies $([\mathrm{A}]/[\mathrm{Rb}])_{\mathtt{pvp}} < 1$, and the desired operating alkali to Rb ratio is never less than 1. Therefore, the mole fraction of the alkali metal will be high, $f_{\mathtt{A}} \geq 0.8$. When this is true or when the coefficient n is much less than 1, we can make approximation $(f_{\mathtt{A}})^n \approx 1$, which allows us to analytically solve for the required mole fraction:

$$\frac{f_{\mathtt{Rb}}}{f_{\mathtt{A}}} \approx \frac{([\mathrm{A}]_{\mathrm{goal}}/[\mathrm{A}]_0)^n}{([\mathrm{Rb}]/[\mathrm{A}])_0} \cdot \left(\frac{[\mathrm{Rb}]}{[\mathrm{A}]}\right)_{\mathrm{goal}} \tag{24}$$

CRC Pure Alkali to Pure Rb Ratio				
	Li	**Na**	**K**	**Cs**
$T_{\mathtt{min}}$ (K)	453.65	370.87	336.53	312.46
$T_{\mathtt{min}}$ (°C)	180.5	97.72	63.38	39.31
$[A]_{\mathtt{min}}$ (1/cm^3)	3.79×10^{6}	3.18×10^{9}	3.23×10^{10}	1.90×10^{11}
$([A]/[Rb])_{\mathtt{min}}$	8.87×10^{-9}	6.06×10^{-4}	0.0727	3.36
$T_{\mathtt{max}}$ (K)	1050	700	600	550
$T_{\mathtt{max}}$ (°C)	777	427	327	277
$[A]_{\mathtt{max}}$ (1/cm^3)	1.81×10^{16}	1.10×10^{16}	1.17×10^{16}	2.12×10^{16}
$([A]/[Rb])_{\mathtt{max}}$	8.68×10^{-4}	0.0301	0.252	1.72
$[A]_0$ (1/cm^3)		10^{14}		
$([Rb]/[A])_0$	16800	112	6.31	0.427
n	0.516	0.259	0.0970	−0.0575

Table 6: Alkali to Rb Pure Vapor Pressure Curve Ratio. These parameters are used in Eqns. (22), (23), & (24). The function is fit to values from the CRC formula [4] over a temperature range that covers the higher melting point to a temperature that corresponds to at least 10^{16} 1/cm^3. The formula reproduces the CRC values to ±3.5% for Li and ±1.0% for all others.

Element	Symbol	Mol. Wgt.	Melting		Boiling	
		g/mol	°C	K	°C	K
Lithium	Li	6.941	180.5	453.65	1342	1615
Sodium	Na	22.989770	97.72	370.87	883	1156
Potassium	K	39.0983	63.38	336.53	759	1032
Rubidium	Rb	85.4678	39.31	312.46	688	961
Cesium	Cs	132.90545	28.44	301.59	671	944
Calcium	Ca	40.078	842	1115	1484	1757
Chlorine	Cl	35.453	-101.5	171.65	-34.04	239.11

Table 7: Physical Properties of Selected Elements. Molecular weights from [3] and temperatures from [4].

Finally, we can use Eqn. (12) to calculate the required operating temperature for the prescribed alkali operating density.

Traditionally for pure Rb cells, the operating temperature is about 190 °C. This corresponds to a Rb density of about 6×10^{14} 1/cm^3. Since the alkali-^{3}He spin exchange rate constants are roughly the same, we'll specify that we want roughly the same total (alkali+Rb) density for the hybrid cells. Tab. (7) lists the molecular weights needed for this method and Tab. (8) lists the required mole fraction ratios for typical hybrid vapor ratios.

2.3 Glovebox Method

In this method, an appropriate amount of Rb is added to approximately one gram of the alkali metal:

$$\frac{\text{mass of Rb}}{\text{mass of A}} = \left(\frac{\text{Mol. Wgt. of Rb}}{\text{Mol. Wgt. of A}}\right)\left[\frac{\mathrm{f}_{\mathtt{Rb}}}{\mathrm{f}_{\mathtt{A}}}\right]_{\text{need}} \tag{25}$$

Because alkali metals are highly reactive to both water vapor and oxygen, the alkali handling is done in a dry N_2 environment within a glovebox. Care is taken to ensure that the glovebox has low levels of contaminants that react with the alkali metals. Both alkali metals are weighed to within 0.3 mg and inserted into an

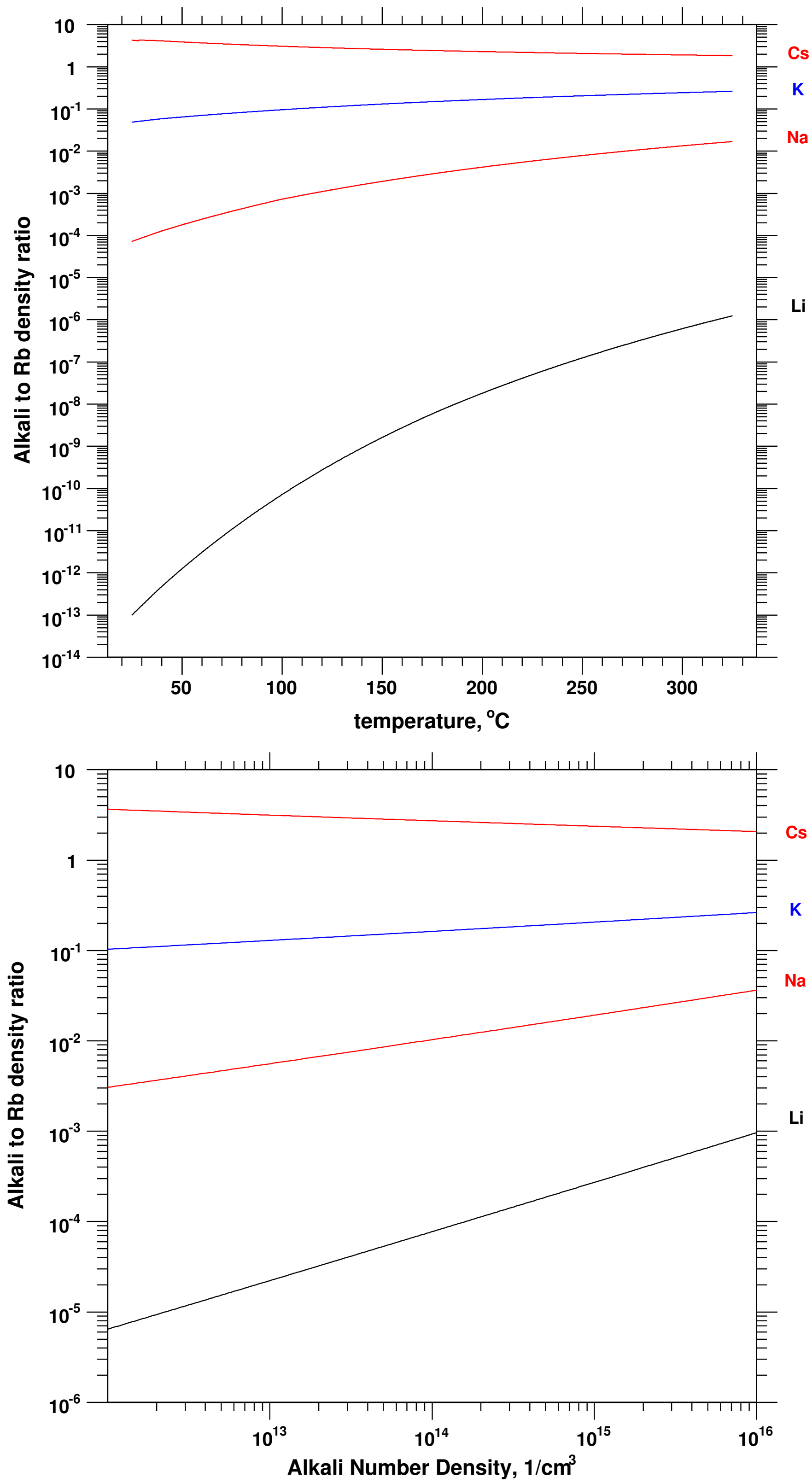

Figure 4: Alkali to Rb pure vapor pressure curve ratio vs. Temperature and Pure Alkali Density. These use the CRC formulas [4].

empty ampuole. The mix is then heated to a temperature above the highest individual melting point of the two metals. The ampuole is then capped with rubber stopper and removed from the glovebox. The ampuole is sealed under the flow of argon gas. Once the ampuole is sealed, it is once again heated above the melting point and vigorously agitated. In theory, the two metals have been melted and mixed together to produce a homogeneous hybrid mix.

2.4 Reaction Method

This method has not been attempted by us because we've found the glovebox method adequate for our purposes. In addition, it is not clear how one determines that all of the alkali salt has been reacted. It is included for completeness. An alternative technique [7, 8] is to reduce appropriate amounts of RbCl and ACl with Calcium chips. The reaction is given by:

$$2\mathrm{ACl} \ + \ \text{excess Ca} \ + \ \text{metal impurities} \stackrel{\text{HEAT}}{\longrightarrow} 2\mathrm{A} \ + \ \mathrm{CaCl_2} \ + \ (\mathrm{Ca} \ + \ \text{metal impurities}) \tag{26}$$

where A is Li, Na, or K. The reaction is catalyzed by heat provided by a flame that is kept under the melting point of Calcium. High vapor pressure impurities are pumped away. The mass ratio of RbCl to ACl needed to produce a necessary ratio of Rb to A in the solid mix is given by:

$$\frac{\text{mass of RbCl}}{\text{mass of ACl}} = \left(\frac{\text{Mol. Wgt. of RbCl}}{\text{Mol. Wgt. of ACl}}\right)\left[\frac{\mathrm{f}_{\mathtt{Rb}}}{\mathrm{f}_{\mathtt{A}}}\right]_{\text{need}} \tag{27}$$

The minimum amount of Calcium to add is obtained from this inequality:

$$\frac{\text{mass of Ca}}{\text{mass of ACl}} \ \geq \ \frac{1}{2}\left(1+\left[\frac{\mathrm{f}_{\mathtt{Rb}}}{\mathrm{f}_{\mathtt{A}}}\right]_{\text{need}}\right)\left(\frac{\text{Mol. Wgt. of Ca}}{\text{Mol. Wgt. of ACl}}\right) \tag{28}$$

Tab. (7) lists molecular weight and melting point data needed for this method and Tab. (8) lists the required mass ratios for typical hybrid vapor rations.

Hybrid Mole Fractions			
	Li	**Na**	**K**
1:1 & 3×10^{14} 1/cm^3			
$f_{\texttt{Rb}}/f_{\texttt{A}}$	1.05×10^{-4}	0.0119	0.176
$m_{\texttt{Rb}}$ (mg)	1.29	44.1	385
$m_{\texttt{RbCl}}/m_{\texttt{ACl}}$	3.00×10^{-4}	0.0246	0.285
$m_{\texttt{Ca}}/m_{\texttt{ACl}}$	0.473	0.347	0.316
$T_{\texttt{op}}$ (K)	843	577	493
$T_{\texttt{op}}$ (°C)	570	303	220
5:1 & 6×10^{14} 1/cm^3			
$f_{\texttt{Rb}}/f_{\texttt{A}}$	3.00×10^{-5}	2.84×10^{-3}	0.0377
$m_{\texttt{Rb}}$ (mg)	0.370	10.6	82.4
$m_{\texttt{RbCl}}/m_{\texttt{ACl}}$	8.56×10^{-5}	5.88×10^{-3}	0.0611
$m_{\texttt{Ca}}/m_{\texttt{ACl}}$	0.473	0.344	0.279
$T_{\texttt{op}}$ (K)	872	596	508
$T_{\texttt{op}}$ (°C)	599	323	235
20:1 & 6×10^{14} 1/cm^3			
$f_{\texttt{Rb}}/f_{\texttt{A}}$	7.50×10^{-6}	7.10×10^{-4}	9.43×10^{-3}
$m_{\texttt{Rb}}$ (mg)	0.0924	2.64	20.6
$m_{\texttt{RbCl}}/m_{\texttt{ACl}}$	2.14×10^{-5}	1.47×10^{-3}	0.0153
$m_{\texttt{Ca}}/m_{\texttt{ACl}}$	0.473	0.343	0.271
$T_{\texttt{op}}$ (K)	872	596	507
$T_{\texttt{op}}$ (°C)	599	323	234

Table 8: Required Mole Fraction Ratios, Mass Ratios, and Operating Temperatures. The mass of Rb is specified assuming an alkali mass of 1 gram. The desired operating hybrid vapor ratios of alkali to Rb are 1:1, 5:1, and 20:1. The difference between these values and ones obtained from a "full" numerical solution is about a few percent.

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