

# Predicted High-Temperature Properties of Rubidium

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A virial equation of state for rubidium with coefficients through the fifth virial is predicted from experimental PVT data of potassium and cesium by application of the thermodynamic similarity principle. Exact thermodynamic relationships involving virial coefficients and other selected literature properties are used to generate saturation and superheat properties of rubidium vapor. Values of enthalpy, entropy, specific heat, and specific volume are tabulated for some 200 selected states in the temperature range from 1300° to 2400° F. and in the pressure range from 0.2 to 28 atm.

THE UNIQUE properties of the liquid alkali metals and their vapors make them attractive as coolants and working fluids in heat pipes, turbines, and other heat transfer systems. These metallic fluids offer the capability of operating at high temperatures to take advantage of the increased thermal efficiency. Design problems associated with new high temperature systems require an improved knowledge of the properties of the metals.

In response to this need, several properties of sodium, potassium, and cesium [including PVT (10), vapor pressure (11), and liquid specific volume (12)] were measured to high temperatures (2300° to 2500° F.) and to high pressure (31 atm.). From the experimental data for each metal, the authors have generated and published consistent sets of thermodynamic properties (4, 5, 6). The present article extends this work to rubidium, without additional measurements, by using the thermodynamic similarity principle.

## COMPRESSIBILITY DATA AND AN EQUATION OF STATE FOR RUBIDIUM

**Interpolation Method.** When the compressibility data of Stone *et al.* (10) for the three alkali metals—sodium, potassium, and cesium—were compared, the authors noted that their molal volumes exhibited consistent behavior. For example, the value of the difference ratio  $(\bar{V}_{Cs} - \bar{V}_K) / (\bar{V}_{Cs} - \bar{V}_{Na})$  was surprisingly constant at all temperature and pressure states within the limiting superheat range of the sodium data. In fact, an average value of 0.20 for this ratio was generally within 10% of all observed values. These observations verified the expected high degree of thermodynamic similarity for the vapors, and the authors reasoned that at any similar state, the volume of rubidium should fall between that of potassium and cesium.

The authors also noted that at any temperature and pressure state the difference between the molal volumes of any two metals was small. For example, the maximum difference, over the superheat range of the sodium data, was less than 7% for sodium and potassium and less than 2% for cesium and potassium. Since the observed volumes of potassium and cesium bracket the desired volume of rubidium and differ themselves by only a small amount, the authors recognized that any reasonably accurate method of interpolating between the values could be used to generate a consistent and reliable set of PVT data for rubidium over a wide temperature range.

One method of interpolation was suggested by the existing tables of computed thermodynamic functions for the monatomic and diatomic gases of the alkali metals. From the tabulated functions for each metal, equilibrium constants of dimerization can be estimated and the molal volume at any state can be computed by assuming that only ideal

monatomic and diatomic species are present. Since the thermodynamic functions were based on spectroscopic heats of dimerization, it appeared likely that molal volumes computed from them would be of sufficient accuracy to permit reliable interpolations. To this end, apparent molal volumes  $\bar{V}$  for the four metals were computed from the tables of Evans *et al.* (3) at a series of pressure and temperature states between 1160° and 2240° F. (the maximum temperature of the tabulated functions).

These computed volumes for sodium, potassium, and cesium were in reasonable agreement with corresponding observed quantities, and exhibited the same thermodynamic similarity noted with the observed data. The authors concluded that a reliable interpolation at any state would be permitted with the equation

$$\bar{V}_{Rb} = \bar{V}_{Cs} - \frac{\bar{V}_{Cs} - \bar{V}_{Rb}}{\bar{V}_{Cs} - \bar{V}_K} (\bar{V}_{Cs} - \bar{V}_K) \quad (1)$$

Values of the ratio  $(\bar{V}_{Cs} - \bar{V}_{Rb}) / (\bar{V}_{Cs} - \bar{V}_K)$  at any given temperature were relatively independent of pressure and showed the expected constancy with temperature. The value varied from 0.58 to 0.45 over the temperature range from 1160° to 2100° F., but tailed off to a value of 0.35 at 2240° F. This higher temperature trend is believed to be due to a breakdown in the assumptions underlying the computation of the thermodynamic functions, and an average value of 0.51 was selected for interpolation at all temperatures.

**Virial Equation of State.** Compressibility factors for rubidium may be calculated with Equation 1 over a considerable superheat range and one could generate virial coefficients and a virial equation of state by the graphical methods described for potassium (5). However, it will be shown that an equivalent equation of state may be obtained by an alternate method in which the coefficients are computed from those observed for potassium and cesium with

$$B_{Rb} = 0.49 B_{Cs} + 0.51 B_K \quad (2)$$

$$C_{Rb} = 0.49 C_{Cs} + 0.51 C_K \quad (3)$$

$$D_{Rb} = 0.49 D_{Cs} + 0.51 D_K \quad (4)$$

$$E_{Rb} = 0.49 E_{Cs} = 294,000 \quad (5)$$

Second, third, and fourth virial coefficients at 50° intervals from 1300° to 2400° F. were computed from these equations, and the values for each coefficient were fitted by the least-squares method with a simple exponential equation. The resulting equation of state is

$$\frac{p\bar{V}}{RT} = 1 + \frac{B}{\bar{V}} + \frac{C}{\bar{V}^2} + \frac{D}{\bar{V}^3} + \frac{E}{\bar{V}^4} \quad (6)$$

where

$$\begin{aligned} \log |B| &= -3.77134 + 4511.9/T + \log T \\ & \quad B < 0 \\ \log C &= 1.90677 + 607.19/T + 5.6975 \times 10^{-6}/T^2 \\ \log |D| &= 4.59913 - 4806.5/T + 11.865 \times 10^{-6}/T^2 \\ & \quad D < 0 \\ E &= 294,000 \end{aligned}$$

The fit of the virial equation of state to the interpolated compressibility data for rubidium was checked mathematically. Compressibility factors for rubidium at states covering the temperature range from 1300° to 2400° F. and the pressure range from 1 to 28 atm. (the limiting pressures of the potassium *PVT* data) were computed by the interpolation method with Equation 1, and these were compared with those computed from the virial equation. The standard deviation at some 300 superheat states was less than  $\pm 0.05\%$ .

#### CALCULATION OF THERMODYNAMIC PROPERTIES AND FUNDAMENTAL DATA

The important properties of the metallic liquid and vapor are volume, enthalpy, entropy, and specific heat. These properties for rubidium were computed from the virial equation of state, from exact thermodynamic relationships, or from the fundamental property equations included in this section.

**Saturation Pressure of Liquid Rubidium.** Several investigators have published vapor pressures of rubidium above 1 atm. Tepper *et al.* (13) reported the equation

$$\log p = 5.72795 - 7110.53/T - 0.14058 \log T \quad (7)$$

which is based on measurements in the range from 830° to 1976° F. His results are generally within 1.2% of those by Achener (1) (881° to 1808° F.) and within 3.3% of those by Bonilla, Sawhney, and Makansi (2) (833° to 1740° F.). Since an extrapolation of the selected equation to 2400° F. is required, the Kirchhoff equation by Tepper was arbitrarily selected because this form of the equation was found by Stone *et al.* (11) to fit the vapor pressures of several alkali metals over wide temperature ranges.

Table I. Summary of Specific-Heat Measurements of Liquid Rubidium

Investigator	Temp. Range, ° F.	Specific-Heat Equation, B.t.u./Lb.-° R.
Achener	150-1650	$c_p^l = 0.11617 - 4.3003 \times 10^{-5} T + 1.299 \times 10^{-7} T^2$
Tepper	260-2000	$c_p^l = 0.0881$

Table II. Saturation Properties of Rubidium

(Basis:  $h = 0$  and  $s = 0$  for solid rubidium at 0° R.)

$t, ^\circ \text{F.}$	$p_s,$ Lb./ Sq. In.	$v_s^l,$ Cu. Ft./Lb.	$v_s^g,$ Cu. Ft./Lb.	$h_s^l,$ B.t.u./Lb.	$\Delta h_s,$ B.t.u./Lb.	$h_s^g,$ B.t.u./Lb.	$s_s^l,$ B.t.u./ Lb.-° F.	$\Delta s_s,$ B.t.u./ Lb.-° F.	$s_s^g,$ B.t.u./ Lb.-° F.
1300.00	17.02	0.01341	11.7204	153.04	337.97	491.01	0.3375	0.1921	0.5295
1400.00	27.85	0.01369	7.4229	161.52	330.92	492.44	0.3421	0.1779	0.5201
1500.00	43.33	0.01399	4.9293	169.99	323.81	493.80	0.3465	0.1652	0.5118
1600.00	64.55	0.01430	3.4099	178.39	316.79	495.18	0.3507	0.1538	0.5045
1700.00	92.65	0.01463	2.4439	186.72	309.97	496.70	0.3546	0.1435	0.4981
1800.00	128.76	0.01499	1.8062	195.07	303.31	498.38	0.3583	0.1342	0.4926
1900.00	173.97	0.01537	1.3700	203.63	296.55	500.18	0.3620	0.1257	0.4877
2000.00	229.33	0.01578	1.0614	212.72	289.21	501.93	0.3657	0.1176	0.4833
2100.00	295.77	0.01622	0.8353	222.79	280.51	503.30	0.3696	0.1096	0.4792
2200.00	374.16	0.01670	0.6634	234.31	269.43	503.74	0.3740	0.1013	0.4753
2300.00	465.24	0.01724	0.5283	247.45	254.92	502.37	0.3787	0.0924	0.4711
2400.00	569.64	0.01783	0.4229	260.14	238.52	498.66	0.3831	0.0834	0.4665

**Density of Liquid Rubidium.** The law of rectilinear diameters was shown by Grosse (7) to be valid for metals over temperature ranges extending from their melting points to their critical points. Thus, the observed liquid densities of Achener (1) in the temperature range from 182° to 1671° F. were fitted with a rectilinear equation

$$\frac{d_s^g + d_s^l}{2} = 50.279 - 0.007365 T \quad (8)$$

using vapor densities from this article. This equation was used to extrapolate liquid densities to 2400° F.

**Specific Volume of Saturated and Superheated Rubidium Vapor.** The value of this property at each state was obtained directly from the virial equation of state.

**Enthalpy, Entropy, and Specific Heat of Saturated and Superheated Rubidium Vapor.** These properties were computed along constant temperature lines from exact thermodynamic relationships with the starting point for a particular property being the value of that property for the monomeric gas at 1 atm. The working relationships presented for potassium (5) may be used for rubidium by expanding them to include terms for the fifth virial.

**Enthalpy, Entropy, and Specific Heat of Monomeric Rubidium Vapor.** The magnitude of each property reported in this article is largely determined by the selected monomeric gas property and the enthalpy of sublimation at absolute zero. Equations for the monomeric gas properties (relative to the solid crystal at 0° R.) are

$$(h^0)^g = 412.36 + 0.058091 T + 1600 e^{-31.930/T} \quad (9)$$

$$(s^0)^g = 0.10994 + 0.133759 \log T + 0.3424 e^{-30.308/T} \quad (10)$$

$$(c_p^0)^g = 0.05809 + 1.609 e^{-28.047/T} \quad (11)$$

These were derived from the work of Evans *et al.* (3) and are based on their tabulated properties over the temperature range from 0° to 3200° R. and on the enthalpy of sublimation at 0° R. (19.58 mean kcal. per gram atom) derived in the next section.

**Enthalpy of Sublimation at 0° R. and the Specific Heat of Liquid Rubidium.** The enthalpy of sublimation is needed to relate the enthalpy of the monomeric gas to the base state, the crystal at 0° R. The virial coefficients of rubidium vapor having been evaluated, a reliable value of the sublimation constant can be obtained from saturation pressure data with the third-law equation

$$\begin{aligned} (\Delta h_0^g)_s = & - \frac{RT}{M_1} \left( \frac{2B}{V} + \frac{3C}{2V^2} + \frac{4D}{3V^3} + \right. \\ & \left. \frac{5E}{4V^4} + \ln p_s - \ln \frac{p_s V}{RT} \right) - T \Delta[(f^0 - h_0^g)/T]_{s,0} \quad (12) \end{aligned}$$



on the specific-heat equation of Achener is preferred, and the average value of 19.58 kcal. per gram atom was selected for the thermodynamic calculations in this article.

**Enthalpy and Entropy of Vaporization of Rubidium.** Latent heats of vaporization were calculated with

$$\Delta h_v = Jp_s(1114.1/T - 0.009566) (v_g^s - v_l^s) \quad (15)$$

which was derived by a differentiation of the vapor-pressure equation of Tepper and subsequent substitution into the Clapeyron equation. A value of  $V_g^s$  at each temperature was obtained from Equation 8 and a value of  $v_g^s$  from the virial equation of state.

The entropy of vaporization at each saturation point

was obtained by dividing the appropriate enthalpy change by the absolute temperature.

**Enthalpy and Entropy of Liquid Rubidium.** These properties of the saturated liquid at each temperature were obtained by subtracting the enthalpy or entropy of vaporization from the corresponding property of the saturated vapor.

### THERMODYNAMIC PROPERTIES AND DISCUSSION

The saturation and superheat properties of rubidium from 1300° to 2400° F. are presented in Tables II and III. They were computed from exact thermodynamic relationships involving the virial and vapor-pressure equations, but sev-

Table III. Thermodynamic Properties of Rubidium Vapor in the Superheat Region (Continued)

(Basis:  $h = 0$  and  $s = 0$  for solid rubidium at 0° R.)

$p$ , P.S.I.	$v_g^s$ , Cu. Ft./ Lb.	$z$ , $p \bar{V}/RT$	$h^g$ , B.t.u./ Lb.	$s^g$ , B.t.u./ Lb.-° F.	$c_p^g$ , B.t.u./ Lb.-° F.	$p$ , P.S.I.	$v_g^s$ , Cu. Ft./ Lb.	$z$ , $p \bar{V}/RT$	$h^g$ , B.t.u./ Lb.	$s^g$ , B.t.u./ Lb.-° F.	$c_p^g$ , B.t.u./ Lb.-° F.
2100° F.						2300° F.					
205.74	1.3048	0.83531	519.60	0.49238	0.1205	308.62	0.9195	0.81898	527.36	0.48750	0.1177
191.05	1.4229	0.84585	522.29	0.49488	0.1168	293.92	0.9752	0.82722	529.36	0.48916	0.1150
176.35	1.5609	0.85647	525.01	0.49753	0.1131	279.22	1.0366	0.83534	531.36	0.49088	0.1123
161.66	1.7241	0.86722	527.77	0.50035	0.1092	264.53	1.1047	0.84339	533.36	0.49266	0.1097
146.96	1.9204	0.87813	530.57	0.50337	0.1052	249.83	1.1808	0.85139	535.36	0.49451	0.1071
132.26	2.1608	0.88923	533.42	0.50665	0.1010	235.14	1.2664	0.85938	537.37	0.49644	0.1046
117.57	2.4618	0.90055	536.31	0.51023	0.0967	220.44	1.3634	0.86737	539.40	0.49847	0.1021
102.87	2.8496	0.91210	539.26	0.51419	0.0923	205.74	1.4743	0.87540	541.44	0.50061	0.0995
88.18	3.3675	0.92389	542.25	0.51865	0.0877	191.05	1.6024	0.88349	543.50	0.50287	0.0969
73.48	4.0937	0.93594	545.28	0.52378	0.0830	176.35	1.7519	0.89165	545.59	0.50527	0.0943
58.78	5.1844	0.94825	548.36	0.52987	0.0782	161.66	1.9289	0.89990	547.69	0.50785	0.0916
44.09	7.0041	0.96081	551.48	0.53747	0.0733	146.96	2.1415	0.90826	549.83	0.51063	0.0888
29.39	10.6463	0.97363	554.64	0.54782	0.0683	132.26	2.4017	0.91675	551.99	0.51364	0.0860
14.70	21.5783	0.98669	557.84	0.56487	0.0632	117.57	2.7273	0.92537	554.18	0.51696	0.0832
11.76	27.0451	0.98934	558.48	0.57024	0.0622	102.87	3.1464	0.93413	556.40	0.52065	0.0802
8.82	36.1568	0.99199	559.12	0.57712	0.0612	88.18	3.7058	0.94304	558.64	0.52482	0.0772
5.88	54.3807	0.99465	559.77	0.58673	0.0602	73.48	4.4898	0.95211	560.92	0.52966	0.0742
2.94	109.0535	0.99732	560.41	0.60303	0.0591	58.78	5.6667	0.96135	563.22	0.53546	0.0710
						44.09	7.6295	0.97076	565.55	0.54276	0.0679
						29.39	11.5572	0.98033	567.91	0.55281	0.0647
						14.70	23.3442	0.99008	570.29	0.56955	0.0614
						11.76	29.2383	0.99205	570.76	0.57487	0.0608
						8.82	39.0621	0.99403	571.24	0.58168	0.0601
						5.88	58.7101	0.99601	571.72	0.59123	0.0595
						2.94	117.6548	0.99800	572.21	0.60746	0.0588
						2400° F.					
						411.49	0.6867	0.78698	525.89	0.48161	0.1264
						396.79	0.7196	0.79520	527.79	0.48294	0.1229
						382.10	0.7548	0.80317	529.65	0.48429	0.1198
						367.40	0.7925	0.81094	531.47	0.48566	0.1169
						352.70	0.8333	0.81853	533.27	0.48707	0.1143
						338.01	0.8774	0.82598	535.05	0.48850	0.1118
						323.31	0.9254	0.83330	536.82	0.48998	0.1094
						308.62	0.9779	0.84052	538.58	0.49150	0.1072
						293.92	1.0355	0.84767	540.34	0.49307	0.1050
						279.22	1.0992	0.85477	542.10	0.49470	0.1028
						264.53	1.1698	0.86184	543.86	0.49640	0.1007
						249.83	1.2488	0.86889	545.63	0.49816	0.0986
						235.14	1.3376	0.87595	547.41	0.50001	0.0965
						220.44	1.4383	0.88303	549.20	0.50196	0.0944
						205.74	1.5535	0.89015	551.01	0.50401	0.0922
						191.05	1.6864	0.89732	552.84	0.50619	0.0901
						176.35	1.8417	0.90455	554.68	0.50851	0.0879
						161.66	2.0254	0.91187	556.54	0.51100	0.0856
						146.96	2.2460	0.91927	558.43	0.51369	0.0833
						132.26	2.5159	0.92678	560.33	0.51661	0.0810
						117.57	2.8537	0.93439	562.26	0.51983	0.0786
						102.87	3.2883	0.94212	564.21	0.52343	0.0762
						88.18	3.8684	0.94998	566.19	0.52751	0.0738
						73.48	4.6811	0.95796	568.18	0.53225	0.0713
						58.78	5.9010	0.96609	570.20	0.53795	0.0687
						44.09	7.9352	0.97435	572.25	0.54515	0.0661
						29.39	12.0055	0.98275	574.31	0.55509	0.0635
						14.70	24.2200	0.99130	576.40	0.57173	0.0609
						11.76	30.3277	0.99303	576.82	0.57702	0.0603
						8.82	40.5075	0.99476	577.24	0.58381	0.0598
						5.88	60.8675	0.99650	577.66	0.59334	0.0593
						2.94	121.9482	0.99825	578.08	0.60956	0.0587
						2300° F.					
411.49	0.6351	0.75424	512.33	0.47678	0.1466						
396.79	0.6678	0.76469	514.68	0.47827	0.1406						
382.10	0.7025	0.77461	516.93	0.47976	0.1355						
367.40	0.7395	0.78409	519.11	0.48126	0.1312						
352.70	0.7793	0.79321	521.23	0.48278	0.1273						
338.01	0.8222	0.80202	523.30	0.48432	0.1239						
323.31	0.8687	0.81060	525.34	0.48589	0.1207						

eral factors regarding the basic data should be recognized when using the tabulated properties. The virial equation was obtained by interpolation between the experimental PVT data of potassium and cesium. Its experimental basis is, therefore, determined by the potassium data which cover a pressure range from 2 to 28 atm. and a temperature range from 1600° to 2500° F. The saturated vapor-pressure equation of Tepper represents data covering a pressure range of 0.04 to 14.6 atm. and a temperature range of 830° to 1976° F. Properties of rubidium vapor have been included in the tables for some states which are outside the measured limits of the basic data, and these properties may be of reduced accuracy.

Tepper *et al.* (14) have recently derived thermodynamic properties for rubidium to a temperature of 2060° F. from experimental compressibility data, and the properties may be compared with those generated in this article. If the NRL data are arbitrarily taken as reference and the property changes from  $p_s$  to 0.5 atm. are compared at temperatures covering the overlapping range, the enthalpy changes reported by Tepper *et al.* are 56% high, 4% low, and 26% low at temperatures of 1880°, 1700°, and 1520° F., respectively, and their entropy changes at the same temperatures are 12% high, 5% low, and 12% low. The observed discrepancies in the two sets of properties can be explained by the precision of the data by Tepper *et al.* (14). In fact, the random errors in their compressibility factors range from 1 to 3% and are larger than the differences which exist between the observed compressibility factors of potassium and cesium (5, 6) between which the rubidium values are interpolated.

The authors believe that the properties generated from the calculated equation of state are practically equivalent to those which would have been obtained if experimental compressibilities had been measured. This statement is based on the evidence presented for the thermodynamic similarity of the alkali metal vapors and on the reliability check obtained by comparing computed values for the specific heat of the liquid with corresponding experimental quantities. Specific-heat values based on monomeric gas properties (see preceding section) may be computed directly from the enthalpy values for the liquid (Table II). These are shown in Table IV to be in good agreement with the corresponding experimental values of Achener (1). The significance of this can be readily missed. One must recognize, first, that the specific heats computed from monomeric gas properties are completely independent of the experimental values, even though the corresponding enthalpy values are directly related by the third-law equation used to obtain  $(\Delta H_s^0)_l$ . One must also recognize that the computed specific-heat values and all the properties of rubidium in Tables II and III are dependent upon the same three basic relationships—the enthalpy equation for the monomeric gas, the virial equation of state, and the

vapor-pressure equation. Therefore, the observed agreement in the specific-heat values tends to substantiate these basic relationships and to increase the degree of confidence which can be placed in the reported values for all the properties.

## NOMENCLATURE

$B$	= second virial coefficient, cu. ft./mole
$C$	= third virial coefficient, (cu. ft.) <sup>2</sup> /(mole) <sup>2</sup>
$D$	= fourth virial coefficient, (cu. ft.) <sup>3</sup> /(mole) <sup>3</sup>
$E$	= fifth virial coefficient, (cu. ft.) <sup>4</sup> /(mole) <sup>4</sup>
$c_p$	= specific heat at constant pressure, B.t.u./lb.-° F.
$d$	= density, lb./cu. ft.
$f$	= free energy, B.t.u./lb.
$h$	= enthalpy per unit mass, B.t.u./lb.
$\Delta h_v$	= enthalpy change upon vaporization of a unit mass of equilibrium vapor, B.t.u./lb.
$\Delta H_v$	= enthalpy change upon vaporization of a mole of equilibrium vapor, B.t.u./mole
$J$	= any unit conversion
$M_i$	= molecular weight of monomeric species
$p$	= absolute pressure, p.s.i.a.
$R$	= gas constant
$s$	= entropy per unit mass, B.t.u./lb.-° F.
$T$	= absolute temperature, ° R.
$t$	= temperature, ° F.
$V$	= molal volume (per formula weight of monomer), cu. ft./mole
$v$	= specific volume, cu. ft./lb.
$z$	= compressibility factor, $pV/RT$

## Subscripts

0	= quantity at 0° R.
$p$	= constant pressure
$s$	= quantity at saturation
K	= quantity for potassium
Na	= quantity for sodium
Rb	= quantity for rubidium
Cs	= quantity for cesium

## Superscripts

$g$	= quantity in gas state
$l$	= quantity in liquid state
o	= standard state, 1 atm. for gas

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Table IV. Comparison of Experimental Specific-Heat Values of Saturated Liquid Rubidium with Those by the Monomeric Gas Path

Temperature, ° F.	Monomeric Gas Path, $c_p^b$ , B.t.u./Lb.-° F.	Experimental Values of Achener, <sup>a</sup> $c_p^l$ , B.t.u./Lb.-° F.
1300	0.0846	0.0808
1400	0.0848	0.0812
1500	0.0844	0.0818
1600	0.0836	0.0828
1700	0.0832	(0.0838)
1800	0.0842	(0.0854)

<sup>a</sup> Experimental values in parenthesis are extrapolated.

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