

Thermodynamic Properties of the Alkali Metals

William H. Evans, Rosemary Jacobson,¹ Thomas R. Munson,² and Donald D. Wagman

The available data on the thermodynamic properties of the elements lithium, sodium, potassium, rubidium, and cesium have been analyzed, and selected values of these properties are presented in tabular form. The tables include values of the free-energy function, $(F^\circ - H_0^\circ)/T$; heat-content function, $(H^\circ - H_0^\circ)/T$; entropy, S° ; heat content, $(H^\circ - H_0^\circ)$; heat capacity, C_p° ; heat of formation, ΔH_f° ; free energy of formation, ΔF_f° ; and logarithm of the equilibrium constant of formation, $\log K_f$, for the solid, the liquid, and the monatomic and diatomic gases as a function of temperature from 0° K to high temperatures.

1. Introduction

As part of a general program on the collection, analysis, and compilation of data on the chemical thermodynamic properties of chemical substances [1, 2],³ a survey has been made of all of the available data relating to the thermodynamic properties of the alkali metals, lithium, sodium, potassium, rubidium, and cesium. There is considerable interest in the use of these metals in chemical syntheses, as well as in their use as heat-transfer media. A large amount of new data has become available since the early summaries of Gordon [3] and Kelley [4, 5]; it is believed that a complete summary of the data on these elements presented in a convenient tabular form will be very useful to engineers, physicists, and chemists engaged in problems involving these substances. This survey will also indicate gaps and weaknesses in the present state of our knowledge with respect to these substances and indicate areas requiring additional research.

2. Units and Standard States

The calorie used in these calculations is the thermochemical calorie, defined by the relation: 1 cal = 4.1840 abs j. The other constants are those given by Wagman et al. [6]. The ice point, 0° C, is taken as 273.16° K [7]. The chemical atomic weights [8] used are: Li, 6.940; Na, 22.991; K, 39.10; Rb, 85.48; Cs, 132.91. For gases the standard state chosen is the hypothetical ideal gas at 1-atmosphere pressure. For solids and liquids the standard state is taken as the substance under 1-atmosphere pressure (or saturated vapor pressure, if this is greater). As is customary, nuclear spin and isotopic mixing contributions to the free-energy function and entropy are omitted; all values are for the naturally occurring isotopic mixture. The symbols used for thermodynamic quantities are those used previously [1, 2].

¹ Present address: Department of Chemistry, University of Michigan, Ann Arbor, Mich.

² Present address: The Vitro Corporation, West Orange, N. J.

³ Figures in brackets indicate the literature references at the end of this paper.

3. Calculation of the Thermodynamic Functions

3.1. Monatomic Gases

The translational contributions to the thermodynamic functions of the monatomic gases Li, Na, K, Rb, and Cs were calculated by use of the equations given by Wagman et al. [6] (corrected for the new definition of the thermochemical calorie). The additional contributions due to electronic excitation are easily obtained in terms of the partition function, Q , and the derived functions Q' and Q''

$$Q = \sum_i g_i e^{-\epsilon_i/kT}$$

$$Q' = \sum_i g_i (\epsilon_i/kT) e^{-\epsilon_i/kT}$$

$$Q'' = \sum_i g_i (\epsilon_i/kT)^2 e^{-\epsilon_i/kT}$$

These contributions were evaluated by direct summation. The energy levels, ϵ_i , and multiplicities, g_i , were taken from Moore [9]. The factor hc/k , used to convert wave numbers to degrees, was taken as 1.43847. From these, the electronic contributions to the thermodynamic functions are easily obtained

$$-(F^\circ - H_0^\circ)/T = R \ln Q$$

$$(H^\circ - H_0^\circ)/T = R(Q'/Q)$$

$$C^\circ = R[Q''/Q - (Q'/Q)^2]$$

3.2. Diatomic Gases

The translational contributions to the thermodynamic functions for the diatomic molecules Li₂, Na₂, K₂, Rb₂, and Cs₂ were evaluated with the same equations used for the monatomic gases. The rotational and vibrational constants given in table 1 were used to calculate the thermodynamic functions for a rigid rotator [6] with moment of inertia, I , equal to $h/[8\pi^2 c B_e(1 - \alpha_e/2)]$, and symmetry number 2, and for an independent harmonic oscillator [10] with a fundamental frequency of $(\omega_e - 2x_e\omega_e)$.⁴

⁴ The spectroscopic notation is that used by Herzberg [12].

TABLE 1. Molecular constants ^a

	Li ₂	Na ₂	K ₂	Rb ₂	Cs ₂
10 ⁸ r _e , cm	2.672 ₅	3.078 ₅	3.923	4.12 _b	4.46 _{5b}
B _e , cm ⁻¹	0.67272	0.15471	0.05622	0.0231 _{5b}	0.0127 _{5b}
α _e , cm ⁻¹	0.00702	0.00078	0.000219	0.000058 ^c	0.000035 ^c
ω _e , cm ⁻¹	351.43 ₅	159.23	92.64	57.28	41.990
xω _e , cm ⁻¹	2.592	0.726	0.354	0.096 ^d	0.08005
10 ⁸ D ₀ , cm ⁻¹	986.	58.4	8.3	1.5 ^e	0.47 ^e
10 ⁸ B ₀ , cm ⁻¹	28.	0.5	0.08	-----	-----

^a Values from Herzberg [12], except as noted.^b Estimated by a Badger's rule extrapolation [13].^c Estimated from $\alpha_e = \frac{6B_e^2}{\omega_e} \left[\left(\frac{x_e \omega_e}{B_e} \right)^{1/2} - 1 \right]$ [12, pp. 90-115].^d Given erroneously as 0.96 by Herzberg; see Tsi-Ze and San-Tsiang [14], and Kusch [15].^e These values are for $D_e = D_0 - \frac{1}{2}\beta$. Estimated from $D_e = 4B_e^3/\omega_e^3$ [12, p. 90].

Mayer and Mayer [11], using an expression for the internal energy of the diatomic molecule that includes the effect of rotational stretching, vibrational anharmonicity, and rotational-vibrational interaction, have obtained equations giving the corrections to the rigid rotator-harmonic oscillator approximation. Starting with the same expression for the energy, we have obtained similar correction equations, in a somewhat more convenient form

$$-\frac{(F^\circ - H_0^\circ)}{RT} \text{ corr} = \frac{8\gamma^2}{\sigma} + \frac{\delta}{(e^u - 1)} + \frac{2x_e u}{(e^u - 1)^2}$$

$$\frac{(H^\circ - H_0^\circ)}{RT} \text{ corr} = \frac{8\gamma^2}{\sigma} + \frac{\delta e^u}{(e^u - 1)^2} + \frac{4x_e u e^u}{(e^u - 1)^3} - \frac{2x_e u}{(e^u - 1)^2}$$

$$\frac{C^\circ}{R} \text{ corr} = \frac{16\gamma^2}{\sigma} - \frac{\delta e^u u^2}{(e^u - 1)^2} + \frac{2\delta e^{2u} u^2}{(e^u - 1)^3} - \frac{8x_e u^2 e^u}{(e^u - 1)^3} - \frac{4x_e u^3 e^u}{(e^u - 1)^3} + \frac{12x_e u^3 e^{2u}}{(e^u - 1)^4}$$

In these equations $\sigma = (B_e - \frac{1}{2}\alpha_e)hc/kT$, $u = (\omega_e - 2x_e\omega_e)hc/kT$, $\delta = \alpha_e/B_e$, and $4\gamma^2 = D_e/B_e$.

With these equations, corrections were calculated at 250°, 300°, 500°, 1,000°, and 1,500° K; values at intermediate temperatures were obtained by linear interpolation. The corrections⁵ at 1,500° K are tabulated in table 2.

TABLE 2. Corrections added to the thermodynamic functions for the rigid rotator-harmonic oscillator at 1,500° K

	(F° - H ₀ °)/T	(H° - H ₀ °)/T	C _p ^o
	cal/deg mole	cal/deg mole	cal/deg mole
Li ₂ -----	-0.207	0.237	0.482
Na ₂ -----	-0.267	.287	.575
K ₂ -----	-0.351	.369	.740
Rb ₂ -----	-0.321	.330	.660
Cs ₂ -----	-0.435	.445	.889

⁵ It will be noted that the corrections do not increase smoothly with increasing molecular weight; this irregularity is primarily due to the values of x_e , which are also not smooth. More precise spectroscopic measurements are necessary before it can be decided whether this is a real effect.

3.3. Solids and Liquids

Thermodynamic functions for the solid and liquid metals were calculated from published experimental low- and high-temperature heat-capacity and heat-content data. The low-temperature data, represented as heat capacities, were plotted as a function of temperature on a large-scale graph, and the "best" curve was drawn through the points. Values of the heat capacity were read off at even temperatures. Numerical integration, using Simpson's rule, gave values of $H_{T_2} - H_{T_1}$; integration of C/T gave values of $S_{T_2} - S_{T_1}$. The observed heat capacities at the lowest temperatures were fitted to a Debye function; this was used to evaluate $S_{T_1} - S_0$ and $H_{T_1} - H_0$ at either 25° or 50° K. The free-energy function, $(F_T - H_0)/T$, was obtained from the relation $(F_T - H_0)/T = (H_T - H_0)/T - S_T$.

The high-temperature data, usually in the form of $H_T - H_{273.16}$, were converted to $(H_T - H_0)/T$, using the values of $H_{273.16} - H_0$ from the low-temperature data. These values were plotted as a function of temperature on a large scale plot, the "best" curve was drawn, and values were read off at even temperatures. These values of $(H_T - H_0)/T$ were smoothed to obtain the final values of $(H_T - H_0)/T$ and $H_T - H_0$. Numerical integration of $(H_T - H_0)/T^2$ gave $-(F_T - H_0)/T$.

To obtain the values of the heat capacity at high temperatures, the smoothed values of $H_T - H_0$ were fitted to an equation of the form

$$(H_T - H_0) = A + BT + CT^2 + D/T.$$

In fitting this equation the heat content and heat capacity at 300° K, selected from the low-temperature data, were used to eliminate the constants A and D . The remaining constants were then evaluated by least squares from the high-temperature heat-content data. This procedure gave an equation that joined the high-temperature heat-content data smoothly to the data obtained from the low-temperature measurements of heat capacity.

The data used in evaluating the thermodynamic functions for solid and liquid lithium are the heat-capacity and heat-content measurements of Simon and Swain* [16],⁶ Laemmel [17], Bernini [18], Koref [19], Dewar [20], Cabbage [21], Yaggee and Untermeyer [22], Bates and Smith* [23], Kleiner and Thum [24], Redmond and Lones* [25], Huchler [98], Douglas et al.* [26], and Carpenter, Harle, and Steward [27]. The reported data on the temperature of the melting point and the heat of fusion are summarized in table 3. The "best" value selected for the heat of fusion, 722.8 cal/mole at 180.54° C, was obtained from the heat-content curves for the solid and liquid.

For sodium the heat-content and heat-capacity data used are given by Koref [19], Dewar [20], Simon and Zeidler* [33], Günther [34], Eastman and Rodebush* [35], Bernini [36], Estreicher and Staniewski [37], Rengade [38, 39], Griffiths* [40], Ginnings, Douglas, and Ball* [41], Dixon and Rodebush [42], Iitaka [43], Pickard and Simon* [91], Schüz [92], Nordmeyer [93], and Nordmeyer and Bernoulli

⁶ The asterisk (*) in each case indicates sources of data given greatest weight.

TABLE 3. Melting point and heat of fusion of lithium

Observer	Temperature	Heat of fusion	Method
	^o C	cal/mole	
Douglas et al. [26].....	180.54	717.1	Heat content ^a
Kilner [28].....	179	690	Do.
Binayendra [29].....	-----	720	No details available
Thum [30].....	180.0	277	Heat content ^a
Kelley [5].....	-----	1,100	Freezing point lowering ^b
Losana [31].....	180.2	-----	-----
Ruff and Johannsen [32].....	180.0	-----	-----
Huchler [97].....	179.5	690	Heat content ^a
Selected value.....	180.54	722.8	-----

^a From measurements of the heat contents of the solid and liquid.

^b From phase studies of binary systems.

[94]. The low-temperature measurements of Pickard and Simon indicate a small "hump" in the heat-capacity curve at about 7° K. This "hump" has not been confirmed by other measurements. As there have been no corresponding "humps" reported for the other alkali metals, the small effect ($\Delta H=0.14$ cal/mole; $\Delta S=0.019$ cal/deg mole) has been omitted in the present calculations; this will permit direct comparison with the other alkali metals. The melting-point and heat-of-fusion data are summarized in table 4. The "best" value selected for the heat of fusion, 621.8 cal/mole at 97.82° C, was obtained from the heat-content curves for the solid and liquid.

TABLE 4.—Melting point and heat of fusion of sodium

Observer	Temperature	Heat of fusion	Method
	^o C	cal/mole	
Bernini [36].....	97.6	410	Heat content ^a
Rengade [38, 39].....	97.90	626.1	Do.
Griffiths [40].....	97.61	634.0	Do.
Ginnings, Douglas, and Ball [41].....	97.80	622.2	Do.
Itaka [43].....	-----	598.0	Do.
Bridgman [44].....	97.63	645	Clapeyron equation ^b
Joannis [45].....	96.5	730	Heat content ^a
Douglas et al. [46].....	^d 97.82	-----	-----
Ladenburg and Thiele [47].....	97.8	-----	-----
Tammann [48].....	97.8	-----	-----
Van Rossen Hoogendijk van Bleiswijk [49].....	97.5	-----	-----
Edmondson and Egerton [50].....	97.7	-----	-----
Kelley [5].....	-----	640	Freezing point lowering ^c
Losana [31].....	97.7	-----	-----
Goria [95].....	97.7	-----	-----
Grube and Schmidt [96].....	98.0	-----	-----
Selected value.....	^d 97.82	621.8	-----

^a From measurements of the heat contents of the solid and liquid.

^b From measurements of the change in melting point with pressure.

^c From phase studies of binary systems.

^d Triple point.

The heat-content and heat-capacity data used for potassium are those of Dewar [20], Simon and Zeidler* [33], Eastman and Rodebush* [35], Bernini [36], Estreicher and Staniewski [37], Rengade [38, 39], Dixon and Rodebush [42], Douglas et al.* [46], Schüz [92], and Carpenter and Steward* [51]. In table 5 are summarized the reported data on the melting point and heat of fusion of potassium. The "best" value selected for the heat of fusion, 554.0 cal/mole at 63.2° C, was obtained from the heat-content curves for the solid and liquid.

TABLE 5.—Melting point and heat of fusion of potassium

Observer	Temperature	Heat of fusion	Method
	^o C	cal/mole	
Bernini [36].....	62.0	530	Heat content ^a
Rengade [38, 39].....	63.50	574	Do.
Bridgman [44].....	63.1	505	Clapeyron equation ^b
Joannis [45].....	58	615	Heat content ^a
Douglas et al. [46].....	^c 63.2	557.9	Do.
Edmondson and Egerton [50].....	63.65	-----	-----
Carpenter and Steward [51].....	63.35	568	Heat content ^a
Smith [52].....	63.6	-----	-----
Selected value.....	^c 63.2	554.0	-----

^a From measurements of the heat contents of the solid and liquid.

^b From measurements of the change in melting point with pressure.

^c Triple point.

The available data on rubidium and cesium are not extensive enough to permit a reliable calculation of the thermodynamic functions for the solid and liquid metals. Dewar [20], Rengade [38, 39], and Deuss [53] have made some measurements on rubidium. Dewar [20], Rengade [38, 39], and Eckardt and Graefe [54] have studied cesium.

4. Selection of the Heats and Free Energies of Formation

The reference state for computing heats and free energies of formation for the various lithium, sodium, and potassium compounds is taken as the solid or liquid metal, depending upon the temperature. Because the thermodynamic functions for solid and liquid rubidium and cesium have not been calculated, the reference state is taken as the monatomic gas for these elements.

The heat of vaporization for a solid or liquid can be calculated from vapor-pressure measurements by the relation

$$-R \ln P = \Delta F_v^0 / T = (\Delta H_v^0)_v / T + \Delta[(F^0 - H_v^0) / T]_v,$$

where P is the vapor pressure in atmospheres at the absolute temperature T , and $(\Delta H_v^0)_v$ is the heat of vaporization at 0° K. This equation is strictly true only if the pressure is so low that the vapor behaves as an ideal gas. If the vapor phase consists of more than one molecular species, all in equilibrium with the condensed phase, P must be replaced by the partial pressure of the species for which the heat of vaporization is desired, and the appropriate thermodynamic functions used.

In the case of the alkali metals, where diatomic molecules are present in the vapor in significant amounts, the vapor pressures reported must be corrected for the effect of the dimer before the heat of vaporization to the monatomic gas (heat of atomization) can be calculated. This correction requires a knowledge of the equilibrium $X_2(g) = 2X(g)$. (X is any alkali metal). If the dissociation energy $D_0^0 (= \Delta H_0^0)$ is known for the diatomic molecule, values of the

equilibrium constant $K = P_X^2/P_{X_2}$ can be calculated from the relation

$$-R \ln K = \Delta F^\circ/T = D_0^\circ/T + \Delta[(F^\circ - H_0^\circ)/T].$$

This assumes that the pressures are so low that the gases are nearly ideal. To obtain values of the ratio $P_{X_2}/P_X = \epsilon$, which is used in the corrections, from these values of K , the total pressure of the system is needed. In the present case this is the total vapor pressure of the metal. Unfortunately, the total vapor pressures reported for the alkali metals, when measured by an effusion or transpiration method, had been calculated assuming a monatomic gas; these pressures must be corrected by an amount dependent upon the method of measurement used. As a first approximation, the pressures reported were used in a $\log P - 1/T$ plot and values of the pressure read from a smooth curve. These total pressures were then used to calculate values of ϵ . The values of ϵ were in turn used to correct the vapor pressures (see below) and the revised vapor pressures, P_π , were replotted and used to calculate new values of ϵ . In general, only one such approximation was necessary.

The correction to be made to the reported vapor-pressure data varies with the method of measurement used. In the following discussion P_1 is the vapor pressure of monatomic X and P_2 that of the dimer, X_2 . P_0 is the reported "total vapor pressure" calculated, assuming a monatomic vapor and P_π is the true total vapor pressure, equal to $P_1 + P_2$. Dalton's law of partial pressures and the ideal gas law are assumed.

In the Knudsen effusion method, which is used for low pressures, the mass of sample lost through a hole of known size in a given time is measured. The molecular weight of the gas escaping is needed to evaluate the pressure; if the gas consists of several molecular species, these must be considered separately. For a given experiment

$$P_1 = \frac{m_1}{at} \sqrt{\frac{2\pi RT}{M_x}} = \frac{m_1 k}{\sqrt{M_x}},$$

where k includes all terms that do not depend upon the molecular weight of the gas. R is the gas constant, a the area of the hole, T the absolute temperature, t the total time of effusion, and m_1 the mass of sample lost as monatomic gas of molecular weight M_x . Likewise, in the same run, for the dimer X_2 ,

$$P_2 = \frac{m_2 k}{\sqrt{M_{X_2}}} = \frac{m_2 k}{\sqrt{2M_x}}.$$

The reported "vapor pressure," calculated from the total loss, $m_1 + m_2$, is

$$P_0 = \frac{(m_1 + m_2)k}{\sqrt{M_x}}.$$

These may be combined to give an expression for P_π as a function of P_0 and ϵ

$$P_\pi = \left(\frac{1 + \epsilon}{1 + \sqrt{2}\epsilon} \right) P_0.$$

In the transpiration or air-saturation method, the amount of material required to saturate a known volume, V , of inert gas at a known total pressure is determined. If the molecular weight of the vapor is known, the vapor pressure can be calculated

$$P_1 = \frac{m_1 RT}{M_x V} \quad P_2 = \frac{m_2 RT}{M_{X_2} V}$$

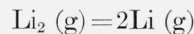
$$P_0 = \frac{(m_1 + m_2) RT}{M_x V}$$

$$P_\pi = \left(\frac{1 + \epsilon}{1 + 2\epsilon} \right) P_0.$$

In the static method, which includes boiling-point measurements, the total pressure exerted by all the gases present is measured, independently of the molecular weight of the gases. Hence no correction to the reported values is necessary.

The values of ϵ and P_π thus obtained were used to obtain the partial pressures of the gas, $P_1 = P_\pi/(1 + \epsilon)$; these were used to calculate $(\Delta H_0^\circ)_v$.

The available vapor-pressure data for lithium must be corrected for the effects of the Li_2 present. To obtain the values of K necessary for this correction, a value of $D_0^\circ(\text{Li}_2)$ is required. Gaydon [55], from various spectroscopic data, has selected 1.12 ± 0.05 ev, or 25.83 ± 1.15 kcal/mole. Lewis [56] measured the relative amounts of diatomic and monatomic molecules directly with his molecular-beam method; if his values of ϵ are combined with total vapor pressures obtained from a large scale $\log P - 1/T$ plot, an average value of D_0° of 25.68 ± 0.15 kcal/mole is obtained.⁷ The average was taken as the "best" value for



$$\Delta H_0^\circ = 25.76 \pm 0.10 \text{ kcal.}$$

The various sets of vapor-pressure data, when corrected, gave the values of $(\Delta H_0^\circ)_v$ listed in table 6. The lithium used by Bogros was apparently impure (see the discussion by Maucherat [60]); the values of $(\Delta H_0^\circ)_v$ calculated from his data show a decided trend with temperature. Lewis' results are seriously in error, probably because he assumed that a calibration for his apparatus from the vapor-pressure data for sodium could be used or because his lithium was impure. A weighted average of Hartmann and Schneider's and Maucherat's values (weighted in-

⁷ All values given for uncertainties, unless otherwise indicated, are our estimates of the over-all uncertainties.

TABLE 6. Heat of vaporization of lithium

Observer	Method	Number of experiments	Temperature	${}^a(\Delta H_0^\circ)_v$
			$^\circ K$	<i>kcal/mole</i>
Lewis [56].....	Knudsen.....	5	852 to 926	35.89 \pm 0.04
Bogros [57, 58].....	do.....	8	732 to 845	38.490 \pm 0.136
Maucherat [59, 60].....	do.....	17	735 to 870	38.162 \pm 0.049
Hartmann and Schneider [61].....	Static.....	8	1,204 to 1,353	38.011 \pm 0.016

^a The uncertainty given is the probable error of the mean.

TABLE 7. Heat of vaporization of sodium

Observer ^a	Method	Number of experiments	Temperature	$(\Delta H_0^\circ)_v$
			$^\circ K$	<i>kcal/mole</i> ^b
*Ladenburg and Thiele [47].....	Transpiration.....	6	615 to 771	25.894 \pm 0.006
*Thiele [63] ^c	do.....	16	614 to 772	25.899 \pm 0.004
*Edmondson and Egerton [50].....	Knudsen.....	4	496 to 570	25.970 \pm 0.008
Heycock and Lamplough [64].....	Static.....	1	1,156	25.749
Hackspill [65, 66].....	do.....	4	623 to 670	25.980 \pm 0.096
Ruff and Johannsen [67].....	do.....	1	1,151	25.641
*Rodebush and Henry [68].....	do.....	29	537 to 670	25.948 \pm 0.005
*Rodebush and Walters [69].....	do.....	14	937 to 1,113	25.830 \pm 0.010
*Haber and Zisch [70].....	Transpiration.....	4	746 to 838	26.036 \pm 0.003
Weiler [71] ^d	Optical.....	10	520 to 590	25.910 \pm 0.061
*Rodebush and DeVries [72].....	Knudsen.....	5	455 to 534	25.961 \pm 0.009
Do.....	Static.....	5	787 to 870	25.704 \pm 0.009
Ladenburg and Minkowski [73] ^d	Optical.....	21	509 to 695	25.899 \pm 0.017
Gebhardt [74].....	Static.....	20	653 to 843	Not calculated
von Wartenberg [75].....	do.....	1	718	26.868
*Makanski, Muendel, and Selke [76].....	do.....	4	1,169 to 1,201	25.757 \pm 0.010
Krafft [77].....	do.....	1	1,015	Not calculated

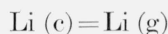
^a The asterisk indicates sources of data given greatest weight.

^b The uncertainty given is the probable error of the mean.

^c Apparently the detailed report of the measurements summarized in [47].

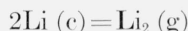
^d Depends upon other sodium vapor-pressure data for calibration.

versely as the probable error) was taken as the best value



$$\Delta H_0^\circ = 38.05 \pm 0.10 \text{ kcal.}$$

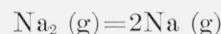
This gives



$$\Delta H_0^\circ = 50.34 \pm 0.23 \text{ kcal.}$$

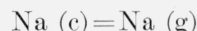
The vapor-pressure data for sodium must be corrected for the Na_2 present. Two values are available for the dissociation energy of Na_2 . The molecular-beam data of Lewis [56] give a $D_0^\circ(\text{Na}_2)$ of 16.91 ± 0.35 kcal. Spectroscopic data, as summarized by Gaydon [55] and Herzberg [12], give D_0° as 17.53 ± 0.15 kcal. The data of Jewett [62] on gas densities are not precise enough to give an accurate value; an approximate value of 20 ± 5 kcal can be obtained from them. In an attempt to decide between the molecular-beam and spectroscopic values, values of ϵ were calculated with each value and used to calculate values of $(\Delta H_0^\circ)_v$ from the various sets of vapor-pressure data. If the correct value of $D_0^\circ(\text{Na}_2)$ has been used and the other data are correct, a constant value for $(\Delta H_0^\circ)_v$ will be obtained. In this case, however, both values of D_0° , as well as an assumed value of 18.20 kcal, gave sets of values of $(\Delta H_0^\circ)_v$ that showed a trend with temperature. The variation of this

trend with increasing values of D_0° indicates that a value of about 19 kcal would be required to give a constant value for $(\Delta H_0^\circ)_v$. The spectroscopic data, though, appear to rule out such a high value. As a "best" value the spectroscopic value was taken



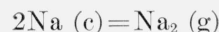
$$\Delta H_0^\circ = 17.53 \pm 0.15 \text{ kcal.}$$

If this value is used for the dissociation energy of Na_2 , the various sets of vapor-pressure measurements give the values of $(\Delta H_0^\circ)_v$ tabulated in table 7. The vapor-pressure data of Gebhardt were completely at variance with all the others and were not considered further. The high-pressure data were not considered to be too reliable because the assumption of ideal gases is not valid. The optical data were given little weight. As a "best" value for the heat of vaporization the weighted average of the starred values was chosen



$$\Delta H_0^\circ = 25.92 \pm 0.05 \text{ kcal.}$$

This value leads to



$$\Delta H_0^\circ = 34.31 \pm 0.18 \text{ kcal.}$$

The vapor-pressure data for potassium were corrected as were those for sodium. Spectroscopic data, as summarized by Herzberg [12], give a $D_0^\circ(\text{K}_2)$ of 11.85 ± 0.10 kcal. The molecular-beam data of Lewis [56] give 12.67 ± 0.50 kcal. As in the case of sodium, the vapor-pressure data did not make possible a choice between these values for the dissociation energy; the spectroscopic value was chosen

$$\text{K}_2(\text{g}) = 2\text{K}(\text{g})$$

$$\Delta H_0^\circ = 11.85 \pm 0.10 \text{ kcal.}$$

With this value, the vapor-pressure measurements gave the values of $(\Delta H_0^\circ)_v$ summarized in table 8. The optical data were given little consideration, because they depend on a calibration using vapor-pressure data from other investigations. The weighted average of the starred values gives

$$\text{K}(\text{c}) = \text{K}(\text{g})$$

$$\Delta H_0^\circ = 21.71 \pm 0.08 \text{ kcal.}$$

This value gives

$$2\text{K}(\text{c}) = \text{K}_2(\text{g})$$

$$\Delta H_0^\circ = 31.57 \pm 0.13 \text{ kcal.}$$

For rubidium D_0° was taken from the spectroscopic data as summarized by Herzberg [12]

$$\text{Rb}_2(\text{g}) = 2\text{Rb}(\text{g})$$

$$\Delta H_0^\circ = 11.30 \pm 0.30 \text{ kcal.}$$

Vapor-pressure data for rubidium are given by Edmondson and Egerton [50], Hackspill [65, 66], Ruff and Johannsen [67], Killian [80], and Scott [82]. Lack of free-energy functions for the solid and liquid prevents calculation of $(\Delta H_0^\circ)_v$. Hence, Rb (g) is taken as the standard state, with $\Delta H_f^\circ = 0$, and

$$2\text{Rb}(\text{g}) = \text{Rb}_2(\text{g})$$

$$\Delta H_0^\circ = -11.30 \pm 0.30 \text{ kcal.}$$

For cesium, D_0° from Herzberg [12] gives

$$\text{Cs}_2(\text{g}) = 2\text{Cs}(\text{g})$$

$$\Delta H_0^\circ = 10.38 \pm 0.30 \text{ kcal.}$$

Vapor-pressure data are given for cesium by Hackspill [65, 66], Ruff and Johannsen [67], Kröner [79], Scott [82], Füchtbauer and Bartels [83], Bartels [84], Langmuir and Kingdon [85, 86], and Taylor and Langmuir [87]. As is the case with rubidium, lack of thermal data for the solid and liquid prevents calculation of $(\Delta H_0^\circ)_v$. Hence, Cs (g) is taken as the standard state, with $\Delta H_f^\circ = 0$, and

$$2\text{Cs}(\text{g}) = \text{Cs}_2(\text{g})$$

$$\Delta H_0^\circ = -10.38 \pm 0.30 \text{ kcal.}$$

5. Discussion

The thermodynamic functions calculated as outlined above are given in tables 9 to 21. The uncertainties in the functions are estimated to be not more than about 20 in the last figure given; the heat contents, $H^\circ - H_0^\circ$, however, as quantities derived directly from the heat-content functions, may retain one additional significant figure for consistency.

Tables 9 to 21 also include values of the heat of formation, ΔH_f° , free energy of formation, ΔF_f° , and logarithm of the equilibrium constant of formation, $\log K_f$, as a function of temperature. These are calculated from the relations

$$\Delta H_f^\circ = \Delta H_f^\circ + \Delta(H^\circ - H_0^\circ)$$

$$\Delta F_f^\circ = \Delta H_f^\circ + T\Delta[(F^\circ - H_0^\circ)/T]$$

$$\log K_f = -\Delta F_f^\circ/4.57567T.$$

The values of ΔH_f° used were those selected above. The values of ΔH_f° and ΔF_f° are often given to more significant figures than the basic value at 0° K to retain differences with temperature that are more

TABLE 8.—Heat of vaporization of potassium

Observer ^a	Method	Number of experiments	Temperature	$(\Delta H_0^\circ)_v$
			^o K	kcal/mole ^b
*Edmondson and Egerton [50]	Knudsen	10	373 to 474	21.745 ± 0.003
*Heycock and Lamplough [64]	Static	1	1,035	21.716
Hackspill [65, 66]	do	9	537 to 673	21.342 ± 0.045
Ruff and Johannsen [67]	Static	1	1,031	21.632
Weiler [71]	Optical ^c	77	430 to 628	21.549 ± 0.010
Krafft [77]	Static	1	1,040	21.805
*Neumann and Völker [78]	Effusion ^d	28	418 to 473	21.709 ± 0.001
*Kröner [79]	Static	17	523 to 672	21.663 ± 0.011
Killian [80]	Ion current	{ Equation only }	(325 to 375)	21.651
*Flock and Rodebush [81]	Static	7	679 to 802	21.762 ± 0.002
Do	do	3	1,028 to 1,033	21.609 ± 0.000

^a The asterisk indicates sources of data given greatest weight.

^b The uncertainty given is the probable error of the mean.

^c Depends upon other potassium vapor-pressure data for calibration.

^d Dynamic effusion torsion balance, using two different holes. Independent of molecular weight of gas.

precise than the basic value. As a derived quantity, $\log Kf$ is given to one more decimal place than is ΔFf° .

Benton and Inatomi [88] and Griffel [89] have calculated the thermodynamic functions for monatomic sodium and potassium, respectively. Their values for the free-energy functions agree with ours, when allowance is made for the different fundamental constants used; their values for $(H^\circ - H_0^\circ)/T$ above 1,800° and 1,400° K, and for C_p° above 1,400° and 1,200° K, respectively, are in error because the contribution of the higher electronic-energy levels has been omitted for these functions.

Gordon [3] has calculated the free-energy function, to 2,000° K, for Li_2 , Na_2 , and K_2 ; Benton and Inatomi [88] have calculated all of the thermodynamic functions to 2,600° K for Na_2 ; Griffel [89] has done the same for K_2 . These calculations agree

with ours within the reported uncertainties, if allowance is made for the different sets of fundamental constants used.

Gaydon has recently [90] revised many of his previous selections [55] of the values of gaseous diatomic dissociation energies. These values differ, in part, from those selected here. For lithium, Gaydon has lowered his previously selected value, obtained from spectroscopic data, apparently because of a lower value obtained from molecular-beam data. If the molecular-beam data are reexamined, as has been done here, a value in much better agreement with the spectroscopic value is obtained. For sodium, Gaydon has also selected a value slightly lower than the spectroscopic value we have used; such a low value seems unlikely if the vapor-pressure data are also considered. He has also lowered the spectroscopic value for rubidium.

TABLE 9. Thermodynamic properties of Li (g)

T	$(F^\circ - H_0^\circ)/T$	$(H^\circ - H_0^\circ)/T$	S°	$H^\circ - H_0^\circ$	C_p°	$\Delta Hf^\circ{}^a$	$\Delta Ff^\circ{}^a$	$\log Kf^a$
$^\circ\text{K}$	cal/deg mole	cal/deg mole	cal/deg mole	cal/mole	cal/deg mole	kcal/mole	kcal/mole	
0	0	0	0	0	0	38.05	38.05	-----
50	-19.3052	4.9680	24.2732	248.4	4.9680	38.286	37.089	-162.1127
100	-22.7487	4.9680	27.7167	496.8	4.9680	38.434	35.824	-78.2932
200	-26.1922	4.9680	31.1602	993.6	4.9680	38.498	33.174	-36.2500
250	-27.3008	4.9680	32.2688	1242.0	4.9680	38.477	31.844	-27.8381
273.16	-27.7410	4.9680	32.7090	1357.1	4.9680	38.461	31.231	-24.9867
298.16	-28.1760	4.9680	33.1440	1481.3	4.9680	38.439	30.570	-22.4076
300	-28.2066	4.9680	33.1746	1490.4	4.9680	38.437	30.521	-22.2346
400	-29.6358	4.9680	34.6038	1987.2	4.9680	38.315	27.899	-15.2432
500	-30.7444	4.9680	35.7124	2484.0	4.9680	37.393	25.390	-11.0976
600	-31.6501	4.9680	36.6181	2980.8	4.9680	37.175	23.010	-8.3813
700	-32.4160	4.9680	37.3840	3477.6	4.9680	36.973	20.665	-6.4517
800	-33.0793	4.9680	38.0473	3974.4	4.9680	36.787	18.348	-5.0124
900	-33.6644	4.9680	38.6324	4471.2	4.9680	36.583	16.056	-3.8991
1,000	-34.1879	4.9680	39.1559	4968.0	4.9680	36.390	13.786	-3.0129
1,100	-34.6614	4.9680	39.6294	5464.8	4.9680	36.199	11.535	-2.2919
1,200	-35.0937	4.9680	40.0617	5961.6	4.9680	36.008	9.301	-1.6937
1,300	-35.4913	4.9680	40.4593	6458.4	4.9682	35.818	7.084	-1.1909
1,400	-35.8595	4.9680	40.8275	6955.2	4.9684	35.629	4.882	-0.7621
1,500	-36.2022	4.9681	41.1703	7452.2	4.9688	35.443	2.691	-0.3921
1,600	-36.5229	4.9681	41.4910	7949.0	4.9696	-----	-----	-----
1,700	-36.8241	4.9683	41.7924	8446.1	4.9712	-----	-----	-----
1,800	-37.1080	4.9685	42.0765	8943.3	4.9737	-----	-----	-----
1,900	-37.3767	4.9688	42.3455	9440.7	4.9775	-----	-----	-----
2,000	-37.6315	4.9694	42.6009	9938.8	4.9831	-----	-----	-----
2,100	-37.8740	4.9703	42.8443	10437.6	4.9908	-----	-----	-----
2,200	-38.1053	4.9714	43.0767	10937.1	5.0012	-----	-----	-----
2,300	-38.3264	4.9730	43.2994	11437.9	5.0143	-----	-----	-----
2,400	-38.5380	4.9750	43.5130	11940.0	5.0308	-----	-----	-----
2,500	-38.7411	4.9776	43.7187	12444.0	5.0514	-----	-----	-----
2,750	-39.2160	4.9871	44.2031	13714.5	5.1309	-----	-----	-----
3,000	-39.6505	5.0017	44.6522	15005.1	5.2098	-----	-----	-----
3,250	-40.0516	5.0216	45.0732	16320.2	5.3362	-----	-----	-----
3,500	-40.4274	5.0475	45.4749	17666.2	5.4535	-----	-----	-----

^a Reference state: [Li (c) below 453.70° K; Li (liq) above 453.70° K.

TABLE 10. *Thermodynamic properties of Li (c) and (liq)*

T	$(F^\circ - H_0^\circ)/T$	$(H^\circ - H_0^\circ)/T$	S°	$H^\circ - H_0^\circ$	C_p°	ΔH_f°	ΔF_f°	$\log K_f$
$^\circ K$	<i>cal/deg mole</i>	<i>cal/deg mole</i>	<i>cal/deg mole</i>	<i>cal/mole</i>	<i>cal/deg mole</i>	<i>kcal/mole</i>	<i>kcal/mole</i>	-----
0	0	0	0	0	0	0	0	0
50	-0.079	0.230	0.309	11.5	0.87	0	0	0
100	-0.493	1.124	1.617	112.4	3.10	0	0	0
150	-1.026	2.029	3.055	304.4	4.43	0	0	0
200	-1.810	2.726	4.536	545.2	5.15	0	0	0
250	-2.479	3.259	5.738	814.8	5.61	0	0	0
273.16	-2.776	3.465	6.241	946.5	5.76	0	0	0
298.16	-3.090	3.663	6.753	1092.2	5.91	0	0	0
300	-3.112	3.677	6.789	1103.1	5.92	0	0	0
350	-3.704	4.016	7.720	1405.6	6.18	0	0	0
400	-4.259	4.306	8.565	1722.4	6.50	0	0	0
450	-4.781	4.570	9.351	2056.5	6.86	0	0	0
453.70 (c)	-4.818	4.589	9.407	2082.0	6.88	0	0	0
453.70 (liq)	-4.818	6.183	11.001	2805.2	7.27	0	0	0
500	-5.423	6.282	11.705	3141.0	7.20	0	0	0
600	-6.583	6.426	13.009	3855.6	7.06	0	0	0
700	-7.580	6.506	14.086	4554.2	6.95	0	0	0
800	-8.452	6.559	15.011	5247.2	6.91	0	0	0
900	-9.227	6.598	15.825	5938.2	6.90	0	0	0
1,000	-9.924	6.628	16.552	6628.0	6.89	0	0	0
1,100	-10.557	6.651	17.208	7316.1	6.88	0	0	0
1,200	-11.136	6.670	17.806	8004.0	6.87	0	0	0
1,300	-11.671	6.685	18.356	8690.5	6.86	0	0	0
1,400	-12.167	6.697	18.864	9375.8	6.84	0	0	0
1,500	-12.629	6.706	19.335	10059.0	6.82	0	0	0

 TABLE 11. *Thermodynamic properties of Li₂ (g)*

T	$(F^\circ - H_0^\circ)/T$	$(H^\circ - H_0^\circ)/T$	S°	$H^\circ - H_0^\circ$	C_p°	$\Delta H_f^{\circ a}$	$\Delta F_f^{\circ a}$	$\log K_f^a$
$^\circ K$	<i>cal/deg mole</i>	<i>cal/deg mole</i>	<i>cal/deg mole</i>	<i>cal/mole</i>	<i>cal/deg mole</i>	<i>kcal/mole</i>	<i>kcal/mole</i>	-----
0	0	0	0	0	0	50.34	50.34	0
250	-37.969	7.600	45.569	1900.0	8.444	50.610	42.087	-36.7922
273.16	-38.646	7.676	46.322	2096.8	8.541	50.544	41.300	-33.0430
298.16	-39.294	7.753	47.047	2311.6	8.620	50.467	40.467	-29.6617
300	-39.357	7.758	47.115	2327.4	8.625	50.461	40.400	-29.4311
400	-41.636	8.002	49.638	3200.8	8.825	50.096	37.093	-20.2663
500	-43.442	8.179	51.621	4089.5	8.941	48.148	34.042	-14.8796
600	-44.94	8.31	53.25	4986	9.02	47.61	31.28	-11.392
700	-46.24	8.42	54.66	5894	9.08	47.13	28.59	-8.924
800	-47.36	8.50	55.86	6800	9.13	46.65	25.98	-7.096
900	-48.37	8.58	56.95	7722	9.18	46.18	23.42	-5.686
1,000	-49.28	8.64	57.92	8640	9.22	45.72	20.91	-4.569
1,100	-50.10	8.69	58.79	9559	9.26	45.27	18.46	-3.667
1,200	-50.86	8.74	59.60	10488	9.30	44.82	16.04	-2.920
1,300	-51.56	8.79	60.35	11427	9.34	44.38	13.66	-2.296
1,400	-52.22	8.83	61.05	12362	9.37	43.95	11.30	-1.764
1,500	-52.83	8.86	61.69	13290	9.41	43.51	8.98	-1.309

^a Reference state: Li (c) below 453.70° K; Li (liq) above 453.70° K.

TABLE 12. *Thermodynamic properties of Na (g)*

T	$(F^\circ - H_0^\circ)/T$	$(H^\circ - H_0^\circ)/T$	S°	$H^\circ - H_0^\circ$	C_p°	ΔH_f° ^a	ΔF_f° ^a	$\log K_f$ ^a
$^\circ K$	<i>cal/deg mole</i>	<i>cal/deg mole</i>	<i>cal/deg mole</i>	<i>cal/mole</i>	<i>cal/deg mole</i>	<i>kcal/mole</i>	<i>kcal/mole</i>	-----
0	0	0	0	0	0	25.92	25.92	-----
50	-22.8753	4.9680	27.8433	248.4	4.9680	26.090	24.817	-108.4748
100	-26.3188	4.9680	31.2868	496.8	4.9680	26.099	23.535	-51.4356
150	-28.3331	4.9680	33.3011	745.2	4.9680	26.062	22.260	-32.4324
200	-29.7623	4.9680	34.7303	993.6	4.9680	26.006	21.001	-22.9483
250	-30.8709	4.9680	35.8389	1242.0	4.9680	25.935	19.757	-17.2716
273.16	-31.3111	4.9680	36.2791	1357.1	4.9680	25.899	19.187	-15.3508
298.16	-31.7461	4.9680	36.7141	1481.3	4.9680	25.857	18.574	-13.6146
300	-31.7767	4.9680	36.7447	1490.4	4.9680	25.854	18.530	-13.4986
400	-33.2059	4.9680	38.1739	1987.2	4.9680	25.008	16.169	-8.8341
500	-34.3145	4.9680	39.2825	2484.0	4.9680	24.764	13.988	-6.1140
600	-35.2203	4.9680	40.1883	2980.8	4.9680	24.538	11.854	-4.3178
700	-35.9861	4.9680	40.9541	3477.6	4.9680	24.332	9.757	-3.0462
800	-36.6495	4.9680	41.6175	3974.4	4.9680	24.132	7.688	-2.1003
900	-37.2346	4.9680	42.2026	4471.2	4.9680	23.938	6.544	-1.5891
1,000	-37.7580	4.9680	42.7260	4968.0	4.9680	23.747	5.622	-0.7916
1,100	-38.2315	4.9680	43.1995	5464.8	4.9680	23.547	4.619	-0.3217
1,200	-38.6638	4.9680	43.6318	5961.6	4.9680	23.340	-0.366	0.0667
1,300	-39.0614	4.9680	44.0294	6458.4	4.9680	-----	-----	-----
1,400	-39.4296	4.9680	44.3976	6955.2	4.9681	-----	-----	-----
1,500	-39.7724	4.9680	44.7404	7452.0	4.9681	-----	-----	-----
1,600	-40.0930	4.9680	45.0610	7948.8	4.9683	-----	-----	-----
1,700	-40.3942	4.9681	45.3623	8445.8	4.9687	-----	-----	-----
1,800	-40.6782	4.9681	45.6463	8942.6	4.9694	-----	-----	-----
1,900	-40.9468	4.9682	45.9150	9439.6	4.9706	-----	-----	-----
2,000	-41.2016	4.9684	46.1700	9936.8	4.9725	-----	-----	-----
2,100	-41.4440	4.9686	46.4126	10434.1	4.9752	-----	-----	-----
2,200	-41.6752	4.9690	46.6442	10931.8	4.9792	-----	-----	-----
2,300	-41.8961	4.9696	46.8657	11430.1	4.9846	-----	-----	-----
2,400	-42.1076	4.9703	47.0779	11928.7	4.9918	-----	-----	-----
2,500	-42.3105	4.9714	47.2819	12428.5	5.0011	-----	-----	-----

^a Reference state: Na (c) below 370.98° K; Na (liq) above 370.98° K.

TABLE 13. *Thermodynamic properties of Na (c) and (liq)*

T	$(F^\circ - H_0^\circ)/T$	$(H^\circ - H_0^\circ)/T$	S°	$H^\circ - H_0^\circ$	C_p°	ΔH_f°	ΔF_f°	$\log K_f$
$^\circ K$	<i>cal/deg mole</i>	<i>cal/deg mole</i>	<i>cal/deg mole</i>	<i>cal/mole</i>	<i>cal/deg mole</i>	<i>kcal/mole</i>	<i>kcal/mole</i>	-----
0	0	0	0	0	0	0	0	-----
50	-0.820	1.574	2.394	78.7	3.82	0	0	0
100	-2.471	3.179	5.650	317.9	5.39	0	0	0
150	-3.953	4.018	7.951	602.7	5.93	0	0	0
200	-5.166	4.540	9.706	908.0	6.26	0	0	0
250	-6.220	4.908	11.128	1227.0	6.48	0	0	0
273.16	-6.662	5.045	11.707	1378.1	6.58	0	0	0
298.16	-7.109	5.180	12.289	1544.4	6.74	0	0	0
300	-7.142	5.189	12.331	1556.8	6.75	0	0	0
350	-7.963	5.441	13.404	1904.3	7.22	0	0	0
370.98 (c)	-8.283	5.548	13.831	2058.2	7.46	0	0	0
370.98 (liq)	-8.283	7.224	15.507	2680.0	7.62	0	0	0
400	-8.828	7.248	16.076	2899.2	7.52	0	0	0
500	-10.450	7.281	17.731	3640.5	7.32	0	0	0
600	-11.777	7.272	19.049	4363.2	7.10	0	0	0
700	-12.896	7.236	20.132	5065.2	6.96	0	0	0
800	-13.860	7.203	21.063	5762.4	6.90	0	0	0
900	-14.706	7.170	21.876	6453.0	6.89	0	0	0
1,000	-15.460	7.141	22.601	7141.0	6.93	0	0	0
1,100	-16.140	7.125	23.265	7837.5	7.01	0	0	0
1,200	-16.759	7.118	23.877	8541.6	7.11	0	0	0

TABLE 14. *Thermodynamic properties of Na₂ (g)*

<i>T</i>	$(F^\circ - H^\circ)/T$	$(H^\circ - H^\circ_0)/T$	S°	$H^\circ - H^\circ_0$	C_p°	ΔH_f° ^a	ΔF_f° ^a	$\log K_f^\circ$ ^a
^o K	cal/deg mole	cal/deg mole	cal/deg mole	cal/mole	cal/deg mole	kcal/mole	kcal/mole	-----
0	0	0	0	0	0	34.31	34.31	-----
250	-45.206	8.218	53.424	2054.5	8.903	33.910	26.118	-22.8325
273.16	-45.934	8.277	54.211	2260.9	8.931	33.815	25.402	-20.3236
298.16	-46.661	8.332	54.993	2484.3	8.962	33.705	24.637	-18.0584
300	-46.713	8.337	55.050	2501.1	8.963	33.698	24.581	-17.9073
400	-49.133	8.505	57.638	3402.0	9.041	31.914	21.719	-11.8668
500	-51.043	8.619	59.662	4309.5	9.099	31.338	19.238	-8.4090
600	-52.62	8.70	61.32	5220	9.15	30.80	16.87	-6.145
700	-53.97	8.77	62.74	6139	9.19	30.32	14.59	-4.554
800	-55.15	8.83	63.98	7064	9.24	29.85	12.37	-3.378
900	-56.19	8.87	65.06	7983	9.28	29.39	10.21	-2.479
1,000	-57.13	8.92	66.05	8920	9.32	28.95	8.10	-1.770
1,100	-57.98	8.95	66.93	9845	9.36	28.48	6.04	-1.200
1,200	-58.76	8.99	67.75	10788	9.40	28.01	4.02	-0.732
1,300	-59.48	9.02	68.50	11726	9.44	-----	-----	-----
1,400	-60.15	9.05	69.20	12670	9.47	-----	-----	-----
1,500	-60.77	9.08	69.85	13620	9.51	-----	-----	-----

^a Reference state: Na (c) below 370.98° K; Na (liq) above 370.98° K.TABLE 15. *Thermodynamic properties of K(g)*

<i>T</i>	$(F^\circ - H^\circ)/T$	$(H^\circ - H^\circ_0)/T$	S°	$H^\circ - H^\circ_0$	C_p°	ΔH_f° ^a	ΔF_f° ^a	$\log K_f^\circ$ ^a
^o K	cal/deg mole	cal/deg mole	cal/deg mole	cal/mole	cal/deg mole	kcal/mole	kcal/mole	-----
0	0	0	0	0	0	21.71	21.71	-----
50	-24.4479	4.9680	29.4159	248.4	4.9680	21.826	20.576	-89.9374
100	-27.9017	4.9680	32.8697	496.8	4.9680	21.795	19.334	-42.2539
150	-29.9160	4.9680	34.8840	745.2	4.9680	21.737	18.115	-26.3935
200	-31.3452	4.9680	36.3132	993.6	4.9680	21.666	16.918	-18.4873
250	-32.4538	4.9680	37.4218	1242.0	4.9680	21.584	15.741	-13.7604
273.16	-32.8940	4.9680	37.8620	1357.1	4.9680	21.542	15.201	-12.1619
298.16	-33.3290	4.9680	38.2970	1481.3	4.9680	21.491	14.623	-10.7182
300	-33.3596	4.9680	38.3276	1490.4	4.9680	21.487	14.581	-10.6218
400	-34.7888	4.9680	39.7568	1987.2	4.9680	20.673	12.422	-6.7870
500	-35.8974	4.9680	40.8654	2484.0	4.9680	20.427	10.389	-4.5410
600	-36.8031	4.9680	41.7711	2980.8	4.9680	20.197	8.403	-3.0608
700	-37.5690	4.9680	42.5370	3477.6	4.9680	19.978	6.455	-2.0152
800	-38.2323	4.9680	43.2003	3974.4	4.9680	19.764	4.538	-1.2396
900	-38.8174	4.9680	43.7854	4471.2	4.9680	19.547	2.648	-0.6430
1,000	-39.3409	4.9680	44.3089	4968.0	4.9680	19.324	0.782	-0.1709
1,100	-39.8144	4.9680	44.7824	5464.8	4.9681	-----	-----	-----
1,200	-40.2467	4.9680	45.2147	5961.6	4.9682	-----	-----	-----
1,300	-40.6443	4.9680	45.6123	6458.4	4.9687	-----	-----	-----
1,400	-41.0125	4.9681	45.9806	6955.3	4.9697	-----	-----	-----
1,500	-41.3552	4.9683	46.3235	7452.4	4.9715	-----	-----	-----
1,600	-41.6770	4.9686	46.6456	7949.8	4.9749	-----	-----	-----
1,700	-41.9772	4.9691	46.9463	8447.5	4.9799	-----	-----	-----
1,800	-42.2612	4.9699	47.2311	8945.8	4.9876	-----	-----	-----
1,900	-42.5299	4.9711	47.5010	9445.1	4.9986	-----	-----	-----
2,000	-42.7849	4.9728	47.7577	9945.6	5.0133	-----	-----	-----
2,100	-43.0276	4.9752	48.0028	10447.9	5.0326	-----	-----	-----
2,200	-43.2592	4.9783	48.2375	10952.3	5.0568	-----	-----	-----
2,300	-43.4806	4.9824	48.4630	11459.5	5.0856	-----	-----	-----
2,400	-43.6927	4.9874	48.6801	11969.8	5.1222	-----	-----	-----
2,500	-43.8964	4.9936	48.8900	12484.0	5.1642	-----	-----	-----

^a Reference state: K (c) below 336.4° K; K (liq) above 336.4° K.

TABLE 16. *Thermodynamic properties of K(c) and (liq)*

<i>T</i>	$(F^\circ - H_0^\circ)/T$	$(H^\circ - H_0^\circ)/T$	<i>S</i> ^o	<i>H</i> ^o - <i>H</i> ₀ ^o	<i>C</i> _p ^o	ΔH_f°	ΔF_f°	log <i>Kf</i>
^o K	cal/deg mole	cal/deg mole	cal/deg mole	cal/mole	cal/deg mole	kcal/mole	kcal/mole	
0	0	0	0	0	0	0	0	-----
50	-1.772	2.654	4.426	132.7	4.99	0	0	0
100	-4.141	4.118	8.259	411.8	5.94	0	0	0
150	-5.951	4.788	10.739	718.2	6.28	0	0	0
200	-7.387	5.189	12.576	1037.8	6.50	0	0	0
250	-8.577	5.471	14.048	1367.8	6.71	0	0	0
273.16	-9.066	5.583	14.649	1525.0	6.88	0	0	0
298.16	-9.559	5.703	15.262	1700.4	7.16	0	0	0
300	-9.595	5.711	15.306	1713.3	7.18	0	0	0
336.4 (c)	-10.260	5.909	16.169	1987.8	7.91	0	0	0
336.4 (liq)	-10.260	7.556	17.816	2541.8	7.68	0	0	0
400	-11.569	7.561	19.130	3024.4	7.53	0	0	0
500	-13.255	7.534	20.789	3767.0	7.34	0	0	0
600	-14.625	7.489	22.114	4493.4	7.20	0	0	0
700	-15.776	7.442	23.218	5209.4	7.13	0	0	0
800	-16.767	7.401	24.168	5920.8	7.11	0	0	0
900	-17.637	7.371	25.008	6633.9	7.16	0	0	0
1,000	-18.413	7.354	25.767	7354.0	7.26	0	0	0

TABLE 17. *Thermodynamic properties of K₂ (g)*

<i>T</i>	$(F^\circ - H_0^\circ)/T$	$(H^\circ - H_0^\circ)/T$	<i>S</i> ^o	<i>H</i> ^o - <i>H</i> ₀ ^o	<i>C</i> _p ^o	ΔH_f° ^a	ΔF_f° ^a	log <i>Kf</i> ^a
^o K	cal/deg mole	cal/deg mole	cal/deg mole	cal/mole	cal/deg mole	kcal/mole	kcal/mole	
0	0	0	0	0	0	31.57	31.57	-----
250	-49.552	8.523	58.075	2130.8	9.019	30.965	23.470	-20.5177
273.16	-50.309	8.565	58.874	2339.6	9.038	30.860	22.780	-18.2260
298.16	-51.061	8.606	59.667	2566.0	9.057	30.735	22.026	-16.1450
300	-51.114	8.609	59.723	2582.7	9.058	30.726	21.973	-16.0070
400	-53.608	8.729	62.337	3491.6	9.121	29.013	19.354	-10.5744
500	-55.566	8.813	64.379	4406.5	9.177	28.442	17.006	-7.4332
600	-57.18	8.88	66.06	5328	9.23	27.91	14.77	-5.380
700	-58.55	8.93	67.48	6251	9.28	27.40	12.61	-3.939
800	-59.74	8.98	68.72	7184	9.33	26.91	10.53	-2.877
900	-60.81	9.02	69.83	8118	9.38	26.42	8.52	-2.068
1,000	-61.76	9.06	70.82	9060	9.43	25.92	6.56	-1.433
1,100	-62.62	9.10	71.72	10010	9.48	-----	-----	-----
1,200	-63.42	9.13	72.55	10956	9.53	-----	-----	-----
1,300	-64.15	9.16	73.31	11908	9.58	-----	-----	-----
1,400	-64.83	9.19	74.02	12866	9.63	-----	-----	-----
1,500	-65.46	9.23	74.69	13845	9.68	-----	-----	-----

^a Reference state: K (c) below 336.4° K; K (liq) above 336.4° K.

TABLE 18. *Thermodynamic properties of Rb (g)*

<i>T</i>	$(F^\circ - H_0^\circ)/T$	$(H^\circ - H_0^\circ)/T$	<i>S</i> ^o	<i>H</i> ^o - <i>H</i> ₀ ^o	<i>C</i> _p ^o	ΔH_f°	<i>Ff</i> ^o	log <i>Kf</i>
^o K	cal/deg mole	cal/deg mole	cal/deg mole	cal/mole	cal/deg mole	kcal/mole	kcal/mole	
0	0	0	0	0	0	0	0	-----
50	-26.7896	4.9680	31.7576	248.4	4.9680	0	0	0
100	-30.2331	4.9680	35.2011	496.8	4.9680	0	0	0
150	-32.2474	4.9680	37.2154	745.2	4.9680	0	0	0
200	-33.6766	4.9680	38.6446	993.6	4.9680	0	0	0
250	-34.7852	4.9680	39.7532	1242.0	4.9680	0	0	0
273.16	-35.2254	4.9680	40.1934	1357.1	4.9680	0	0	0
298.16	-35.6604	4.9680	40.6284	1481.3	4.9680	0	0	0
300	-35.6910	4.9680	40.6590	1490.4	4.9680	0	0	0
400	-37.1202	4.9680	42.0882	1987.2	4.9680	0	0	0
500	-38.2288	4.9680	43.1968	2484.0	4.9680	0	0	0
600	-39.1345	4.9680	44.1025	2980.8	4.9680	0	0	0
700	-39.9004	4.9680	44.8684	3477.6	4.9680	0	0	0
800	-40.5637	4.9680	45.5317	3974.4	4.9680	0	0	0
900	-41.1488	4.9680	46.1168	4471.2	4.9680	0	0	0
1,000	-41.6723	4.9680	46.6403	4968.0	4.9680	0	0	0
1,100	-42.1458	4.9680	47.1138	5464.8	4.9681	0	0	0
1,200	-42.5781	4.9680	47.5461	5961.6	4.9683	0	0	0
1,300	-42.9757	4.9681	47.9438	6458.5	4.9689	0	0	0
1,400	-43.3439	4.9682	48.3121	6955.5	4.9701	0	0	0
1,500	-43.6866	4.9684	48.6550	7452.6	4.9724	0	0	0
1,600	-44.0074	4.9687	48.9761	7949.9	4.9764	0	0	0
1,700	-44.3086	4.9693	49.2779	8447.8	4.9827	0	0	0
1,800	-44.5926	4.9703	49.5629	8946.5	4.9920	0	0	0
1,900	-44.8614	4.9718	49.8332	9446.4	5.0051	0	0	0
2,000	-45.1164	4.9739	50.0903	9947.8	5.0227	0	0	0
2,100	-45.3592	4.9767	50.3359	10451.1	5.0456	0	0	0
2,200	-45.5908	4.9805	50.5713	10957.1	5.0743	0	0	0
2,300	-45.8124	4.9853	50.7977	11466.2	5.1096	0	0	0
2,400	-46.0246	4.9914	51.0160	11979.4	5.1520	0	0	0
2,500	-46.2285	4.9988	51.2273	12497.0	5.2021	0	0	0

TABLE 19. *Thermodynamic properties of Rb₂ (g)*

<i>T</i>	$(F^\circ - H_0^\circ)/T$	$(H^\circ - H_0^\circ)/T$	<i>S</i> ^o	<i>H</i> ^o - <i>H</i> ₀ ^o	<i>C</i> _p ^o	ΔH_f°	ΔF_f°	log <i>K_f</i>
^o K	cal/deg mole	cal/deg mole	cal/deg mole	cal/mole	cal/deg mole	kcal/mole	kcal/mole	-----
0	0	0	0	0	0	-11.30	-11.30	-----
250	-54.408	8.688	63.096	2172.0	9.034	-11.612	-7.509	6.5646
273.16	-55.179	8.718	63.897	2381.4	9.048	-11.633	-7.128	5.7032
298.16	-55.944	8.746	64.690	2607.7	9.061	-11.655	-6.715	4.9222
300	-55.998	8.748	64.746	2624.4	9.062	-11.656	-6.685	4.8698
400	-58.527	8.833	67.360	3533.2	9.111	-11.741	-5.015	2.7398
500	-60.505	8.893	69.398	4446.5	9.158	-11.822	-3.324	1.4528
600	-62.13	8.94	71.07	5364	9.20	-11.90	-1.62	0.589
700	-63.51	8.98	72.49	6286	9.25	-11.97	0.10	-0.032
800	-64.71	9.02	73.73	7216	9.29	-12.03	1.83	-0.501
900	-65.78	9.05	74.83	8145	9.34	-12.10	3.57	-0.866
1,000	-66.73	9.08	75.81	9080	9.38	-12.16	5.31	-1.161
1,100	-67.60	9.11	76.71	10021	9.43	-12.21	7.06	-1.403
1,200	-68.39	9.14	77.53	10968	9.47	-12.26	8.82	-1.606
1,300	-69.13	9.17	78.30	11921	9.51	-12.30	10.57	-1.777
1,400	-69.81	9.19	79.00	12866	9.56	-12.34	12.33	-1.925
1,500	-70.44	9.22	79.66	13830	9.60	-12.38	14.10	-2.054

TABLE 20. *Thermodynamic properties of Cs (g)*

<i>T</i>	$(F^\circ - H_0^\circ)/T$	$(H^\circ - H_0^\circ)/T$	<i>S</i> ^o	<i>H</i> ^o - <i>H</i> ₀ ^o	<i>C</i> _p ^o	ΔH_f°	ΔF_f°	log <i>K_f</i>
^o K	cal/deg mole	cal/deg mole	cal/deg mole	cal/mole	cal/deg mole	kcal/mole	kcal/mole	-----
0	0	0	0	0	0	0	0	-----
50	-28.1053	4.9680	33.0733	248.4	4.9680	0	0	0
100	-31.5488	4.9680	36.5168	496.8	4.9680	0	0	0
150	-33.5631	4.9680	38.5311	745.2	4.9680	0	0	0
200	-34.9923	4.9680	39.9603	993.6	4.9680	0	0	0
250	-36.1009	4.9680	41.0689	1242.0	4.9680	0	0	0
273.16	-36.5411	4.9680	41.5091	1357.1	4.9680	0	0	0
298.16	-36.9761	4.9680	41.9441	1481.3	4.9680	0	0	0
300	-37.0067	4.9680	41.9747	1490.4	4.9680	0	0	0
400	-38.4359	4.9680	43.4039	1987.2	4.9680	0	0	0
500	-39.5445	4.9680	44.5125	2484.0	4.9680	0	0	0
600	-40.4502	4.9680	45.4182	2980.8	4.9680	0	0	0
700	-41.2161	4.9680	46.1841	3477.6	4.9680	0	0	0
800	-41.8794	4.9680	46.8474	3974.4	4.9680	0	0	0
900	-42.4645	4.9680	47.4325	4471.2	4.9680	0	0	0
1,000	-42.9880	4.9680	47.9560	4968.0	4.9681	0	0	0
1,100	-43.4615	4.9680	48.4295	5464.8	4.9684	0	0	0
1,200	-43.8938	4.9681	48.8619	5961.7	4.9692	0	0	0
1,300	-44.2914	4.9682	49.2596	6458.7	4.9711	0	0	0
1,400	-44.6597	4.9685	49.6282	6955.9	4.9748	0	0	0
1,500	-45.0024	4.9692	49.9716	7453.8	4.9813	0	0	0
1,600	-45.3232	4.9702	50.2934	7952.3	4.9918	0	0	0
1,700	-45.6246	4.9720	50.5966	8452.4	5.0078	0	0	0
1,800	-45.9088	4.9746	50.8834	8954.3	5.0307	0	0	0
1,900	-46.1779	4.9783	51.1562	9458.8	5.0618	0	0	0
2,000	-46.4333	4.9834	51.4167	9966.8	5.1026	0	0	0
2,100	-46.6766	4.9903	51.6669	10479.6	5.1541	0	0	0
2,200	-46.9089	4.9991	51.9080	10998.0	5.2176	0	0	0
2,300	-47.1315	5.0102	52.1417	11523.5	5.2940	0	0	0
2,400	-47.3449	5.0239	52.3688	12057.4	5.3836	0	0	0
2,500	-47.5503	5.0403	52.5906	12600.8	5.4874	0	0	0

TABLE 21. *Thermodynamic properties of Cs₂ (g)*

<i>T</i>	$(F^\circ - H_0^\circ)/T$	$(H^\circ - H_0^\circ)/T$	<i>S</i> ^o	<i>H</i> ^o - <i>H</i> ₀ ^o	<i>C</i> _p ^o	ΔH_f°	ΔF_f°	log <i>K_f</i>
^o K	cal/deg mole	cal/deg mole	cal/deg mole	cal/mole	cal/deg mole	kcal/mole	kcal/mole	-----
0	0	0	0	0	0	-10.38	-10.38	-----
250	-57.467	8.786	66.253	2196.5	9.081	-10.668	-6.696	5.8538
273.16	-58.246	8.812	67.058	2407.1	9.097	-10.687	-6.327	5.0623
298.16	-59.019	8.836	67.855	2634.5	9.112	-10.708	-5.928	4.3448
300	-59.074	8.838	67.912	2651.4	9.114	-10.709	-5.898	4.2968
400	-61.627	8.915	70.542	3566.0	9.176	-10.788	-4.282	2.3396
500	-63.623	8.973	72.596	4486.5	9.236	-10.862	-2.647	1.1570
600	-65.26	9.02	74.28	5412	9.30	-10.93	-1.00	0.363
700	-66.66	9.06	75.72	6342	9.36	-10.99	0.66	-0.206
800	-67.87	9.10	76.97	7280	9.42	-11.05	2.33	-0.637
900	-68.95	9.14	78.09	8226	9.48	-11.10	4.00	-0.972
1,000	-69.91	9.18	79.09	9180	9.53	-11.14	5.68	-1.243
1,100	-70.79	9.21	80.00	10131	9.59	-11.18	7.37	-1.464
1,200	-71.59	9.25	80.84	11100	9.65	-11.20	9.06	-1.650
1,300	-72.33	9.29	81.62	12077	9.71	-11.22	10.75	-1.807
1,400	-73.02	9.32	82.34	13048	9.77	-11.24	12.44	-1.942
1,500	-73.66	9.35	83.01	14025	9.83	-11.26	14.14	-2.060

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WASHINGTON, January 11, 1955.