NOMENCLATURE

n_{25} = ethane-*n*-pentane system, mole fraction
n_{27} = ethane-*n*-heptane system, mole fraction
n_{57} = *n*-pentane-*n*-heptane system, mole fraction
n_{257} = ethane-*n*-pentane-*n*-heptane system, mole fraction
P_c = critical pressure, p.s.i.a.
T_c = critical temperature, ° R. or ° F.
T_c' = pseudocritical temperature, ° R.

Subscripts

2, 5, 7 = specific components of mixture

ACKNOWLEDGMENT

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LITERATURE CITED

(1) Cummings, L.W.T., Stones, F.W., Volante, M.A., *Ind. Eng. Chem.* **25**, 728 (1963).
(2) Ekiner, Okan, Ph.D. dissertation, Northwestern University, Evanston, Ill., 1965.
(3) Ekiner, Okan, Thodos, George, *Can. J. Chem. Eng.* **43**, 205 (1966).
(4) Ekiner, Okan, Thodos, George, J. CHEM. ENG. DATA **11**, 154 (1966).
(5) Grieves, R.B., Thodos, George, *Ind. Eng. Chem. Fundamentals* **1**, 45 (1962).

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High Temperature Properties of Potassium

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A virial equation of state for potassium with coefficients through the fourth virial is derived from *PVT* data covering a temperature range from 1600° to 2525° F. The equation is used thermodynamically to obtain superheat and saturation properties of the vapor. Values of the enthalpy, entropy, specific volume, and specific heat for some 200 selected states are tabulated in the temperature range from 1400° to 2500° F., and in the pressure range from 2.9 to 499.3 p.s.i.a.

THE ALKALI METALS are being considered as thermodynamic working fluids in advanced power converters, and reliable values of their properties are required. The existing thermodynamic properties for alkali metal vapors have been calculated in most cases from spectroscopic data, vapor-pressure data, and published thermodynamic functions. The agreement among the calculated properties for a given metal is poor and not acceptable. The principal objective at NRL was to determine experimentally for a wide temperature range the important thermodynamic properties of three metal vapors—sodium, potassium, and cesium. This was to be achieved by a thermodynamic reduction of pressure-volume-temperature data. The *PVT* measurements for each metal to 2500° F. have now been published. This article, the fourth in the series, describes the thermodynamic treatment of the potassium *PVT* data and presents the first thermodynamic properties of this metal derived directly from measured compressibilities.

TREATMENT OF *PVT* DATA

Methods. Spectroscopic studies (*4*) have shown that the vapor of an alkali metal contains molecular species with two or more atoms. For a strongly associating vapor, such as that of potassium, the important properties—enthalpy, entropy, and specific heat—may be reduced from *PVT* data by either of two methods. In the first, the gas is treated as a monatomic assembly with all apparent imperfections given by a virial equation of state, and the thermodynamic quantities are obtained as corrections to those of the monatomic gas in terms of the virial coefficients. In the second method, equilibrium constants are derived for the molecular reactions by treating the gas as a mixture of molecular species, and the thermodynamic quantities are derived from the enthalpy changes associated with changes in the molecular composition of the vapor. The latter method, commonly called the quasichemical, generally assumes that all species behave as perfect gases.

While the two methods should be effectively equivalent from the standpoint of obtaining the three properties—enthalpy, entropy, and specific heat—a higher degree of confidence was placed in the well-established thermodynamic relationships of the virial method. The virial equation of state for potassium with coefficients through the fourth virial was obtained from the raw *PVT* data and used to compute enthalpy, entropy, specific volume, and specific heat of potassium vapor.

Derivation of Virial Coefficients. The virial equation of state in the volume expansion form,

$$\frac{p\tilde{V}}{RT} = A + \frac{B}{\tilde{V}} + \frac{C}{\tilde{V}^2} + \frac{D}{\tilde{V}^3} + \dots \tag{1}$$

was chosen for this analysis, and the four coefficients are commonly called the first, second, third, and fourth virial. With this form of the equation, the first virial coefficient theoretically should be unity.

The virial coefficients are temperature-dependent and were derived graphically by plotting functions along constant temperature lines. Compressibility data at 50° temperature intervals were obtained from large-scale plots of the observed data for the nine experiments reported by Stone *et al.* (*9*). Virial coefficients were obtained from these data by a procedure similar to that devised by Hirschfelder, McClure, and Weeks (*7*). The second virial coefficient at each temperature was obtained as the lim $[(z-1)\tilde{V}]_{(1/\tilde{V} \to 0)}$, the third virial as the lim $Q_{(1/\tilde{V} \to 0)}$ where Q is defined as $[(z-1)\tilde{V} - B]\tilde{V}$, and the fourth virial as $dQ/d(1/\tilde{V})$.

It was noted from preliminary plots of z vs. $1/\tilde{V}$ for isotherms covering the temperature range that the deviations of observed compressibility factors from fitted curves were larger for the experiments at low pressures (up to 0.4%) than for those at high pressures (generally less than 0.2%). In addition, the magnitude and sign of the deviation for each experiment were relatively independent of temperature. This behavior can be explained. Nine experiments were used to generate the compressibility data for potassium (*9*). For each of these, pressure was observed as a function of temperature for a given weight of potassium vapor in a constant-volume chamber. Since the larger and principal uncertainties in the low-pressure experiments were generated in the measurement of two temperature-independent quantities (the volume of the chamber and the weight of potassium), the systematic deviations for these experiments were not unexpected.

A knowledge of this systematic behavior was used to help define the temperature dependency of the virial coefficients at lower temperatures. The procedure required the selection of a reference isotherm having the maximum pressure range of the observed compressibility factor in order to obtain the maximum definition of the virial coefficients. Accordingly, a reference temperature of 2450° F. was selected. The compressibility factor, z, at this temperature was plotted as a function of $1/\tilde{V}$, and the second virial coefficient was obtained as the lim $[dz/d(1/\tilde{V})]_{(1/\tilde{V} \to 0)}$. Also, $(z - 1)\tilde{V}$ was plotted as a function of $1/\tilde{V}$ and another value of B was obtained as the lim $[(z - 1)V]_{(1/\tilde{V} \to 0)}$. The most consistent value of B obtained by both procedures was −18.447. Using the value, function Q was calculated and plotted against $1/\tilde{V}$ (Figure 1) and the best linear curve was obtained by least squares, giving greater weight to the higher pressure data. From the deviation of an experimental Q at 2450° F. from the linear curve, the multiplying factor to z required to correct Q to the curve may be computed. Assuming the errors in the five low-pressure experiments to be largely systematic, adjusted compressibility quantities (identified as z^* or Q^*) were derived for each experiment at all temperatures with the multiplying factor obtained at 2450° F.

Second virial coefficients were obtained from large-scale plots of $(z - 1)\tilde{V}$ *vs.* $1/\tilde{V}$ for isotherms at 50° intervals between 2000° and 2550° F. For the five low-pressure experiments, adjusted values, $(z^* - 1)\tilde{V}$, were included on each plot and were given weight in defining the intercepts at lower temperatures. Third and fourth virial coefficients were obtained by plotting the quantity Q *vs.* $1/\tilde{V}$ for isotherms at 50° intervals between 2150° and 2550° F. The adjusted values of Q^* for the low-pressure experiments were, likewise, included on each plot and given weight in defining the intercepts and slopes at lower temperatures. Additional second virial coefficients in the lower temperature range from 1600° to 1950° F. were obtained by computing the average value of $[(z - 1)\tilde{V} - C/\tilde{V} - D/\tilde{V}^2]$ for the lower pressure experiments on each isotherm. The values of C and D required for these calculations were obtained by extrapolation.

Figure 1 gives a plot of Q *vs.* $1/\tilde{V}$ at 2450° F. for the several experiments which were effective in defining the higher virial coefficients. The vertical line for each Q represents the expected probable error in the quantity. Though the corresponding error in z is normally around 0.20%, that in Q becomes increasingly larger at low pressures (low values of $1/\tilde{V}$) as z approaches unity. This figure may be used to illustrate the adjustment procedure, which was particularly helpful in defining the higher virial coefficients at lower temperatures where the definition provided by the higher pressure data is missing. For example, at 2200° F. the virials had to be determined from data corresponding to that for the five lower pressure experiments in Figure 1. Since errors are systematic with respect to the individual experiments, the relative point spread of the data for the five experiments at 2200° F. is the same as that shown at 2450° F. One could proceed at this temperature to weight the points and to define C and D by a least squares curve. However, when the adjusted values of (Q^*) are plotted, a linear curve is defined which is of somewhat lower slope than that obtained by the least squares fit. The curve with the lower slope should be more correct, since it incorporates information from the data at higher temperatures where greater definition is provided by the several experiments at higher pressures.

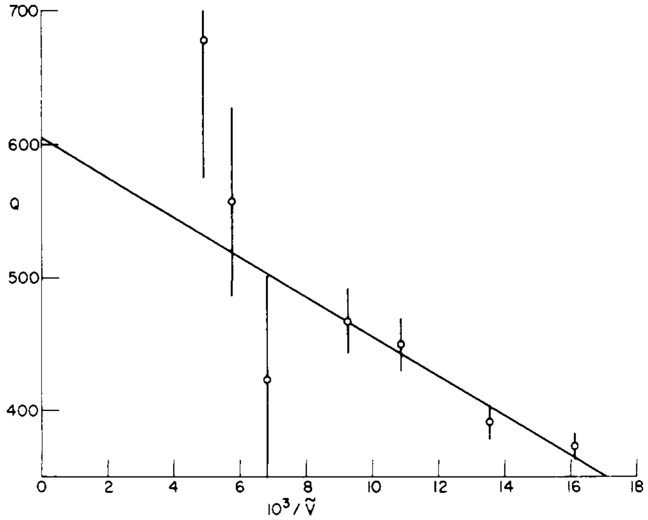

Figure 1. Plot of Q vs. 1/V for potassium at 2450° F.

Virial Equation of State of Potassium. Since the virial coefficients are functions of equilibrium constants (*17*), it is not surprising that each coefficient can be represented for the full temperature range with simple exponential equations. The virial equation of state of potassium is

$$\frac{p\tilde{V}}{RT} = 1 + \frac{B}{\tilde{V}} + \frac{C}{\tilde{V}^2} + \frac{D}{\tilde{V}^3} \tag{2}$$

where

$$\begin{aligned}\log|B| &= -3.8787 + 4890.7/T + \log T \\ &\quad B < 0 \\ \log C &= +0.5873 + 6385.7/T \\ &\quad C > 0 \\ \log|D| &= +1.4595 + 7863.8/T \\ &\quad D < 0\end{aligned}$$

The log T term was included in the equation for the second virial coefficient, since this term can be derived directly from the relationship between the dimerization equilibrium constant and B (*17*).

The fit of the virial equation to observed data is shown graphically in Figure 2, where compressibility isotherms generated from Equation 2 are compared to experimental compressibilities at 100° intervals from 1600° to 2500° F. All the observed compressibility data for potassium as reported by Stone *et al.* (*9*) may be calculated from the virial equation with a standard per cent deviation of ±0.34.

The virial equation of state was effectively derived from experimental data over the temperature range from 2000° to 2525° F. Data were also obtained from 1600° to 2000° F., but the number of experimental points in this region did not permit one to obtain reliable coefficients by the graphical method. Consequently, before the virial equation was acceptable for calculations below 2000° F., it was necessary

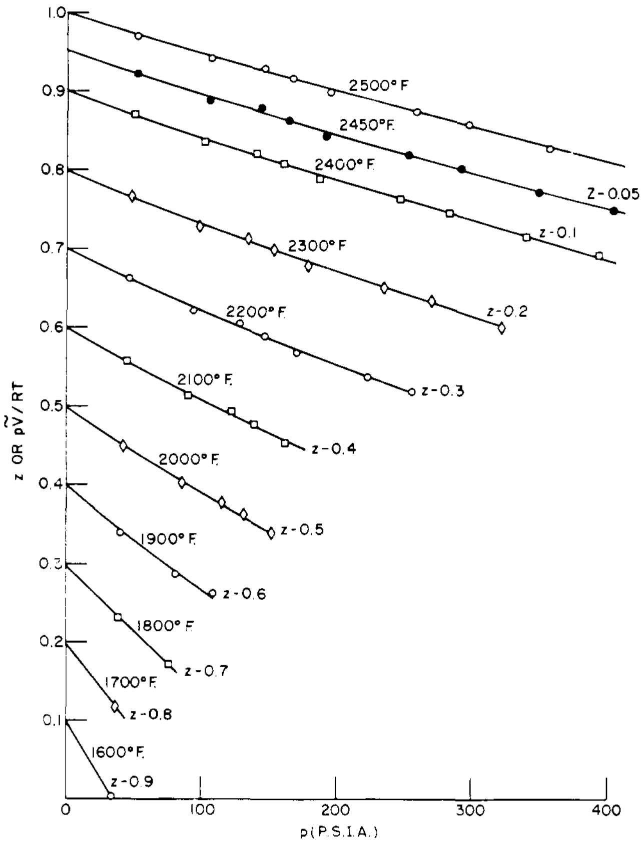

Figure 2. Compressibility of potassium vapor at several temperatures

to determine its fit to the observed lower temperature data. At temperatures and pressures corresponding to observed low-temperature points, compressibility factors were calculated and compared to the observed values. The fit of the virial equation of state to the low-temperature data is illustrated in Figure 2, and found to be equivalent to that obtained at higher temperatures.

FUNDAMENTAL PROPERTIES ON WHICH THERMODYNAMIC PROPERTIES ARE BASED

Saturation Pressure of Liquid Potassium. The vapor-pressure equation of Stone *et al.* (*10*) was chosen, since this equation,

$$\log p = 7.30625 - 8135.3/T - 0.53560 \log T \qquad (3)$$

was based on experimentally determined data over the temperature range from the normal boiling point to 2400° F. and is in good agreement with the lower temperature work of Walling, Nuzum, and Lemmon (*15*) and Makansi *et al.* (*8*).

Specific Volume of Liquid Potassium. The specific volume of the condensed phase was obtained from the equation,

$$\frac{1}{v^l} = 52.768 - 7.4975 \times 10^{-3}t - 0.5255 \times 10^{-6}t^2 + 0.0498 \times 10^{-9}t^3 \qquad (4)$$

which was derived from the observed data of Stone *et al.* and other investigators (*11*). The error limit given for the equation was ±0.6% for the full temperature range from the melting point to 2300° F.

Enthalpy and Entropy of Liquid Potassium. The thermodynamic properties presented in this report are based on the properties of the monomeric gas at 1 atm., but comparison calculations were made using the properties of the saturated liquid as a starting point. The enthalpy and entropy of the liquid (relative to the solid at 0° R.) were computed with

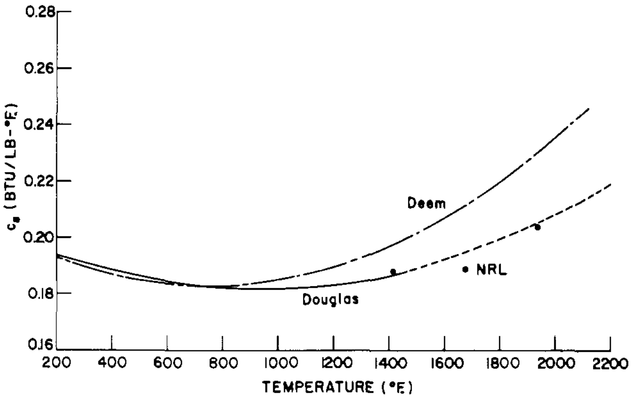

Figure 3. Specific heat of liquid potassium

$$h_s^l = 87.8783 + 0.2022\,t - 0.2177 \times 10^{-4}t^2 + 0.07741 \times 10^{-7}t^3 \qquad (5)$$

$$s_s^l = 0.52298 \log T - 0.64848 \times 10^{-4}T + 0.11589 \times 10^{-7}T^2 - 0.9646 \qquad (6)$$

The equations were derived directly from the work of Douglas *et al.* (*2*) and are based on their specific-heat equation for the solid and liquid over the temperature range from 32° to 1472° F. The enthalpy and entropy of solid potassium at 32° F. were taken from the work of Evans *et al.* (*3*).

The enthalpy and entropy equations were used well beyond the measured limit of the specific-heat data from which they were derived. The selection of the data of Douglas and the validity of the extrapolation of his equation are based on the following information. Three observations of the specific heat of potassium were made from heat-content measurements at NRL in the temperature range from 1300° to 2100° F. The determinations were made in a copper-block calorimeter described by Walker, Grand, and Miller (*13*), and the probable error of each result is ±3%. The three experimental points are compared to the data of Deem, Eldridge, and Lucks (*1*) and Douglas *et al.* (*2*) in Figure 3. The dashed curve above 1472° F. represents a temperature extension of Douglas's data using his specific-heat equation. The NRL data tend to verify this extension, while the smoothed data of Deem diverge at higher temperatures.

Enthalpy and Entropy of Vaporization of Potassium. The latent heat of vaporization was calculated with the equations,

$$\Delta h_v = J\,p_s[1274.6/T_s - 0.036445]\,[v_s^g - v_s^l] \qquad (7)$$

which was derived from Equation 3 and the Clapeyron equation. The value of v_s^l at each temperature was obtained from Equation 4 and the value of v_s^g from the virial equation of state (Equation 2).

The corresponding entropy of vaporization at each saturation point was obtained by dividing the appropriate enthalpy change by the absolute temperature.

Enthalpy, Entropy, and Specific Heat of Monomeric Potassium Vapor. Relationships for these quantities in terms of temperature were derived from the tabulated properties of Evans *et al.* (*3*). The equations for the monomeric gas at 1 atm. (relative to the solid at 0° R.) are:

$$(h^g)^\circ = 998.95 + 0.12700\,T + 24{,}836\,e^{-39{,}375/T} \qquad (8)$$

$$(s^g)^\circ = 0.18075 + 0.12700 \ln T + 0.7617\,e^{-51{,}126/T} \qquad (9)$$

$$(c_p^g)^\circ = 0.12700 + 2.888\,e^{-28{,}070/T} \qquad (10)$$

Enthalpy of Sublimation of Potassium at 0° R. The enthalpy of sublimation at 0° R. is needed to obtain Equation 8, and its value is generally derived from vapor-pressure data. Evans analyzed the low-temperature vapor-pressure measurements existing at that time and selected a value of 21.70 mean kcal. per gram-atom which has been used in this analysis.

The virial equation of state and recent vapor-pressure measurements permit a more positive determination of the sublimation constant. As a check on the value reported by Evans, the vapor-pressure measurements of Stone *et al.* (*10*) were used to compute a new value. The heat of sublimation can be related to the saturation pressure, the virial coefficients, and the free-energy functions using the method outlined by Hicks (*5*), and the resulting relationship is

$$(\Delta H_0^\circ)_v = -RT_s\left[\frac{2B}{\tilde{V}_s} + \frac{3C}{2\tilde{V}_s^2} + \frac{4D}{3\tilde{V}_s^3} + \ln p_s - \ln \frac{p_s\tilde{V}_s}{RT_s}\right] - M_1T_s\left[\frac{f^\circ - h_0^\circ}{T}\right]_l^g \qquad (11)$$

The free-energy functions for the monomeric gas may be obtained from the data of Evans *et al.* (*3*) by using Equations 8 and 9. The free-energy functions for the liquid may be obtained from the heat-capacity data of Douglas *et al.* (*2*) by using Equations 5 and 6.

The functions for the liquid are accurately known to only 1500° F., but Stone *et al.* reported a number of vapor pressures at experimental temperatures below this value. Sublimation values were computed for these experimental pressures, and a value of 21.63 kcal. per gram atom (standard deviation 0.02) was obtained. Within experimental error this verifies the value of 21.70 obtained by Evans and used in this article.

Specific Volume of Saturated and Superheated Vapor. This property at all vapor states (Tables II and III) was computed from the virial equation of state.

Saturated specific volumes were directly observed by Stone *et al.* (*9*). A saturation value was obtained for each of nine *PVT* experiments by a short extrapolation of the superheated vapor curve to the true saturation curve. Specific volumes at temperatures corresponding to these extrapolated points were computed with the virial equation and exhibited an average deviation of only ±0.34%. However, Stone has shown that pressures observed in the vicinity of the intersection of the saturated and superheated vapor curves may be expected to be low (*9*), and it is believed that saturated specific volumes obtained from the virial equation and the vapor-pressure equation are more reliable than those obtained at the intersection points.

CALCULATION OF THERMODYNAMIC PROPERTIES OF POTASSIUM

Basis. The thermodynamic properties of potassium vapor were computed along constant temperature lines. Two computational paths exist for obtaining the properties. The starting point for a particular property along one path is the value of the property for the saturated liquid, and along the other path, the value of the property for the

Table I. Comparison of Monomeric Gas and Liquid Path Calculations

(Virial method)

Temp., °F.	Pressure, P.S.I.A.	Monomeric Gas Path			Liquid Path		
		h^g	s^g	c_p^g	h^g	s^g	c_p^g
1600	29.39	1211.6	1.095	0.260	1199.2	1.090	0.255
	14.70	1236.0	1.140	0.193	1223.5	1.135	0.188
	2.94	1255.6	1.230	0.140	1243.2	1.225	0.135
1800	73.48	1213.3	1.054	0.287	1200.4	1.049	0.290
	14.70	1270.9	1.156	0.160	1258.0	1.151	0.163
	2.94	1282.9	1.242	0.134	1270.1	1.237	0.136
2000	146.96	1219.4	1.026	0.290	1207.6	1.022	0.297
	14.70	1301.3	1.169	0.146	1289.5	1.165	0.153
	2.94	1309.3	1.253	0.131	1297.5	1.249	0.138
2200	249.83	1231.0	1.009	0.283	1220.2	1.005	0.285
	146.96	1270.6	1.046	0.228	1259.8	1.043	0.229
	14.70	1329.6	1.180	0.138	1318.9	1.176	0.140
	2.94	1335.3	1.264	0.129	1324.5	1.260	0.131
2400	396.79	1240.1	0.993	0.293	1227.4	0.989	0.268
	146.96	1312.4	1.062	0.193	1299.7	1.057	0.167
	14.70	1356.9	1.190	0.134	1344.2	1.186	0.109
	2.94	1361.1	1.273	0.129	1348.4	1.269	0.103

Table II. Saturation Properties of Potassium[a]

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

t	p_s	v_l	v_s^g	h^l	Δh_v	h_s^g	s^l	Δs_v	s_s^g
1400.0	15.16	0.02417	30.9931	360.22	828.65	1188.87	0.6688	0.4456	1.1144
1500.0	24.64	0.02469	19.7806	380.05	813.06	1193.12	0.6792	0.4149	1.0941
1600.0	38.16	0.02523	13.2142	399.87	797.40	1197.28	0.6891	0.3871	1.0762
1700.0	56.69	0.02581	9.1829	419.62	781.93	1201.56	0.6984	0.3621	1.0604
1800.0	81.22	0.02641	6.6044	439.32	766.82	1206.14	0.7072	0.3393	1.0466
1900.0	112.76	0.02705	4.8944	459.05	752.06	1211.11	0.7157	0.3187	1.0344
2000.0	152.28	0.02772	3.7229	478.98	737.47	1216.45	0.7239	0.2998	1.0237
2100.0	200.72	0.02844	2.8962	499.37	722.68	1222.05	0.7319	0.2823	1.0143
2200.0	258.93	0.02919	2.2962	520.58	707.06	1227.64	0.7399	0.2658	1.0058
2300.0	327.66	0.02998	1.8487	543.07	689.69	1232.76	0.7481	0.2499	0.9980
2400.0	407.60	0.03083	1.5055	567.51	669.20	1236.71	0.7566	0.2340	0.9907
2500.0	499.30	0.03173	1.2328	595.08	643.12	1238.19	0.7659	0.2173	0.9832

[a] Values are given to more significant figures than the data warrant in order to retain precision in differences.

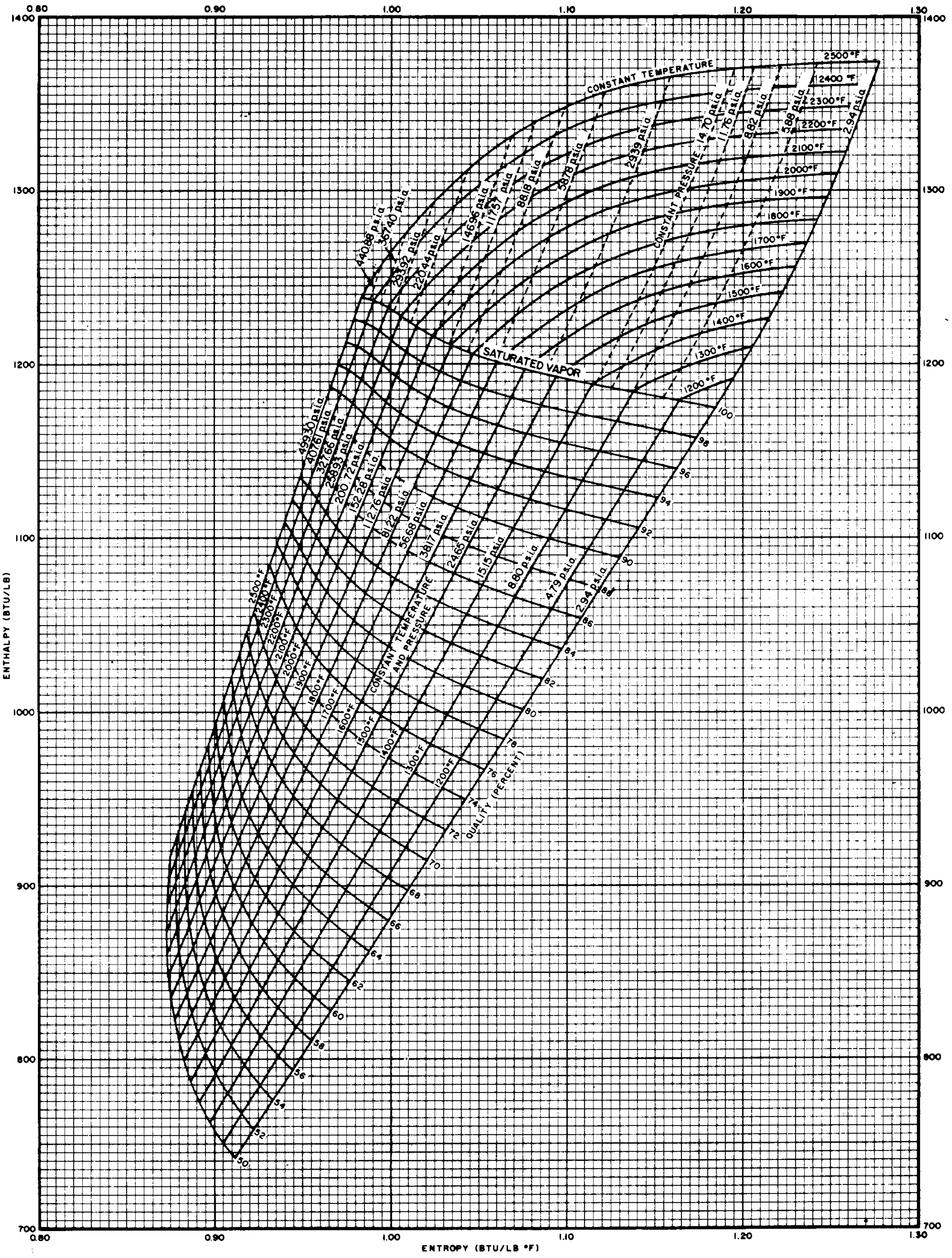

Figure 4. Mollier diagram for potassium

monomeric gas. The two paths are interrelated to a temperature of 1500° F. by the third-law calculation of $(\Delta H_0^0)_v$, but the monomeric gas path is preferred for calculations at higher temperatures for two reasons. First, the specific heat of the vapor and the relative values of both enthalpy and entropy are less dependent upon vaporization quantities. Secondly, the monomeric gas path does not require an extrapolation of the specific heat of the liquid above its measured limit of 1500° F., while the liquid path calculations are subject to considerable error from this standpoint.

Although the thermodynamic properties reported in this article are based on the monomeric gas path, properties by the other path at selected states are used as an internal consistency check. Therefore the thermodynamic relationships and the computational steps for both paths are included in this section. The relationships were derived by an extension of the method described by Hirschfelder (*6*).

Monomeric Gas Path. ENTHALPY, ENTROPY, AND SPECIFIC HEAT OF SATURATED AND SUPERHEATED VAPOR. These properties at all vapor states were computed along isotherms with the following equations:

$$h_i^g = (h^g)^\circ + \frac{RT}{M_1}\left\{\frac{1}{\tilde V}\left[B - T\left(\frac{dB}{dT}\right)\right] + \frac{1}{\tilde V^2}\left[C - \frac{T}{2}\left(\frac{dC}{dT}\right)\right] + \frac{1}{\tilde V^3}\left[D - \frac{T}{3}\left(\frac{dD}{dT}\right)\right]\right\} \tag{12}$$

$$s_i^g = (s^g)^\circ - \frac{R}{M_1}\left\{\ln p - \ln\frac{p\tilde V}{RT} + \frac{B}{\tilde V} + \frac{T}{\tilde V}\left(\frac{dB}{dT}\right) + \frac{C}{2\tilde V^2} + \frac{T}{2\tilde V^2}\left(\frac{dC}{dT}\right) + \frac{D}{3\tilde V^3} + \frac{T}{3\tilde V^3}\left(\frac{dD}{dT}\right)\right\} \tag{13}$$

$$(c_p^g)_i = (c_p^g)^\circ - \frac{R}{M_1} + \frac{R}{M_1}\left\{\frac{\left[1 + \frac{1}{\tilde V}\left(B + T\frac{dB}{dT}\right) + \frac{1}{\tilde V^2}\left(C + T\frac{dC}{dT}\right) + \frac{1}{\tilde V^3}\left(D + T\frac{dD}{dT}\right)\right]^2}{\left[1 + 2\frac{B}{\tilde V} + 3\frac{C}{\tilde V^2} + 4\frac{D}{\tilde V^3}\right]}\right\} - \frac{RT}{\tilde V M_1}\left\{\left(T\frac{d^2B}{dT^2} + 2\frac{dB}{dT}\right) + \frac{1}{2\tilde V}\left(T\frac{d^2C}{dT^2} + 2\frac{dC}{dT}\right) + \frac{1}{3\tilde V^2}\left(T\frac{d^2D}{dT^2} + 2\frac{dD}{dT}\right)\right\} \tag{14}$$

ENTHALPY AND ENTROPY OF CONDENSED PHASE. These properties (Table II) at each temperature were obtained by subtracting the enthalpy and entropy of vaporization from the corresponding properties of the saturated vapor.

Liquid Path. ENTHALPY, ENTROPY, AND SPECIFIC HEAT OF SATURATED VAPOR. The enthalpy and entropy of the saturated vapor at any given temperature were obtained by adding the enthalpy and entropy of vaporization to the corresponding properties of the saturated liquid.

The specific heat at saturation was obtained by numerically evaluating, at 50° intervals, the differential,

$$(c_p^g)_s = \lim\left[\left(\frac{\partial h^g}{\partial T}\right)_p\right]_{(T \to T_s)} = \lim\left[\left(\frac{\Delta h^g}{\Delta T}\right)_p\right]_{(T \to T_s)} \tag{15}$$

ENTHALPY, ENTROPY, AND SPECIFIC HEAT OF SUPERHEATED VAPOR. With the saturated vapor state as a starting point, these properties in the superheat region were computed along constant temperature lines with the following equations:

$$h_i^g = h_s^g - \frac{RT}{M_1}\left\{\frac{1}{\tilde V}\left[B - T\left(\frac{dB}{dT}\right)\right] + \frac{1}{\tilde V^2}\left[C - \frac{T}{2}\left(\frac{dC}{dT}\right)\right] + \frac{1}{\tilde V^3}\left[D - \frac{T}{3}\left(\frac{dD}{dT}\right)\right]\right\}_{\tilde V_i}^{\tilde V_s} \tag{16}$$

$$s_i^g = s_s^g + \frac{R}{M_1}\left\{\ln p - \ln\frac{p\tilde V}{RT} + \frac{B}{\tilde V} + \frac{T}{\tilde V}\left(\frac{dB}{dT}\right) + \frac{C}{2\tilde V^2} + \frac{T}{2\tilde V^2}\left(\frac{dC}{dT}\right) + \frac{D}{3\tilde V^3} + \frac{T}{3\tilde V^3}\left(\frac{dD}{dT}\right)\right\}_{\tilde V_i}^{\tilde V_s} \tag{17}$$

$$(c_p^g)_i = (c_p^g)_s - \frac{R}{M_1}\left\{\frac{\left[1 + \frac{1}{\tilde V}\left(B + T\frac{dB}{dT}\right) + \frac{1}{\tilde V^2}\left(C + T\frac{dC}{dT}\right) + \frac{1}{\tilde V^3}\left(D + T\frac{dD}{dT}\right)\right]^2}{\left[1 + 2\frac{B}{\tilde V} + 3\frac{C}{\tilde V^2} + 4\frac{D}{\tilde V^3}\right]}\right\}_{\tilde V_i}^{\tilde V_s} + \frac{RT}{\tilde V M_1}\left\{\left(T\frac{d^2B}{dT^2} + 2\frac{dB}{dT}\right) + \frac{1}{2\tilde V}\left(T\frac{d^2C}{dT^2} + 2\frac{dC}{dT}\right) + \frac{1}{3\tilde V^2}\left(T\frac{d^2D}{dT^2} + 2\frac{dD}{dT}\right)\right\}_{\tilde V_i}^{\tilde V_s} \tag{18}$$

Comparison of Two Computational Paths. Three properties—enthalpy, entropy, and specific heat—of the superheated vapor were computed by both paths, and values at selected states are compared in Table I. Properties as computed by the two paths exhibit rather good agreement in the temperature range from 1600° to 2200° F., and an internal consistency check of considerable importance is obtained. The basic property relationships, as well as the methods of calculation, are checked by this procedure. It is also interesting in this temperature range to compare values calculated for the specific heat of the liquid (monomeric gas path) with corresponding experimental values (liquid path). Values from the gas path may be obtained directly from h^l in Table II, and these show an average disagreement of only 2.1% (maximum of 3.2%) from those obtained by extending the experimental results of Douglas with his specific-heat equation. This extension to a degree (see Figure 3) is verified by several measurements at NRL.

Values for the specific heat of the liquid when computed from the monomeric gas path are completely independent of the other path, and the agreement between the calculated and observed values increases the degree of confidence which can be placed in the relative values of enthalpy and entropy for the vapor at all saturation and superheat states.

THERMODYNAMIC PROPERTIES OF POTASSIUM AND DISCUSSION

Saturation and superheat properties from 1400° to 2500° F. are presented in Tables II and III, and the thermal properties from 1200° to 2500° F. for both wet and dry vapors are presented graphically in a Mollier chart (Figure 4). Properties of potassium vapor have been included in the tables and in the Mollier diagram for states outside the measured limits of the basic data. For example, superheat properties for states at pressures below 2.3 and above 27.4 atm. required for their computation short extrapolations of the virial equation. Likewise, vaporization and saturation properties at states below 1399° and above 2393° F. (the limits of the saturation data) required short extrapolations of the vapor-pressure equation. The properties computed by extending the basic relationships may be of reduced accuracy.

The properties of potassium in this article were compared to those in two recent publications (*14*), (*16*). The results generated in these studies were not based directly on measured *PVT* data; the properties reported by Walling (*14*) were deduced principally from saturation pressures, and those by Weatherford (*16*) were computed from published thermodynamic functions of the monomeric and

Table III. Thermodynamic Properties of Potassium Vapor in the Superheat Region[a]

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

p	v^g	z	h^g	s^g	c_p^g
		(at 1400° F.)			
15.16	30.9931	0.92035	1188.87	1.11443	0.2840
14.70	32.0491	0.92276	1190.30	1.11664	0.2789
11.76	40.7307	0.93818	1199.36	1.13207	0.2473
8.82	55.2017	0.95363	1208.38	1.15075	0.2163
5.88	84.1450	0.96909	1217.35	1.17538	0.1859
2.94	170.9752	0.98455	1226.27	1.21460	0.1561
		(at 1500° F.)			
24.64	19.7806	0.90620	1193.12	1.09411	0.2936
14.70	34.5370	0.94365	1215.24	1.12972	0.2249
11.76	43.6836	0.95485	1221.78	1.14382	0.2049
8.82	58.9304	0.96609	1228.31	1.16119	0.1851
5.88	89.4273	0.97737	1234.83	1.18454	0.1655
2.94	180.9234	0.98867	1241.34	1.22250	0.1461
		(at 1600° F.)			
38.16	13.2142	0.89203	1197.28	1.07620	0.2999
29.39	17.6188	0.91605	1211.64	1.09517	0.2602
14.70	36.8319	0.95750	1236.01	1.14006	0.1931
11.76	46.4452	0.96593	1240.91	1.15334	0.1797
8.82	62.4699	0.97440	1245.81	1.16991	0.1664
5.88	94.5227	0.98290	1250.72	1.19245	0.1532
2.94	190.6872	0.99144	1255.62	1.22961	0.1401
		(at 1700° F.)			
56.69	9.1829	0.87818	1201.56	1.06043	0.3028
44.09	12.1516	0.90382	1217.02	1.07897	0.2651
29.39	18.8544	0.93490	1235.47	1.10647	0.2196
14.70	39.0051	0.96704	1254.25	1.14871	0.1733
11.76	49.0857	0.97357	1258.03	1.16147	0.1640
8.82	65.8890	0.98014	1261.82	1.17750	0.1547
5.88	99.4983	0.98673	1265.62	1.19952	0.1455
2.94	200.3319	0.99335	1269.42	1.23615	0.1362
		(at 1800° F.)			
81.22	6.6044	0.86487	1206.14	1.04659	0.3024
73.48	7.3986	0.87657	1213.27	1.05417	0.2873
58.78	9.4908	0.89956	1227.16	1.07039	0.2574
44.09	12.9912	0.92350	1241.43	1.09003	0.2260
29.39	20.0101	0.94830	1256.03	1.11578	0.1935
14.70	41.0980	0.97384	1270.89	1.15625	0.1604
11.76	51.6461	0.97902	1273.88	1.16864	0.1537
8.82	69.2279	0.98423	1276.89	1.18432	0.1470
5.88	104.3940	0.98947	1279.90	1.20598	0.1404
2.94	209.8969	0.99472	1282.91	1.24226	0.1337
		(at 1900° F.)			
112.76	4.8944	0.85213	1211.11	1.03443	0.2994
102.87	5.4367	0.86357	1218.10	1.04139	0.2867
88.18	6.4719	0.88114	1228.78	1.05275	0.2667
73.48	7.9273	0.89940	1239.78	1.06566	0.2455
58.78	10.1178	0.91834	1251.08	1.08075	0.2232
44.09	13.7780	0.93792	1262.65	1.09922	0.2000
29.39	21.1116	0.95810	1274.45	1.12376	0.1761
14.70	43.1360	0.97881	1286.46	1.16299	0.1517
11.76	54.1514	0.98302	1288.88	1.17514	0.1468
8.82	72.5119	0.98724	1291.31	1.19057	0.1419
5.88	109.2347	0.99147	1293.75	1.21198	0.1369
2.94	219.4070	0.99573	1296.19	1.24801	0.1320
		(at 2000° F.)			
152.28	3.7229	0.83980	1216.45	1.02372	0.2950
146.96	3.8799	0.84460	1219.38	1.02644	0.2903
132.26	4.3800	0.85812	1227.61	1.03435	0.2770
117.57	5.0075	0.87205	1236.06	1.04296	0.2631
102.87	5.8172	0.88644	1244.74	1.05245	0.2484
88.18	6.9006	0.90131	1253.66	1.06308	0.2329
		(at 2000° F. Cont.)			
73.48	8.4217	0.91665	1262.80	1.07521	0.2166
58.78	10.7088	0.93247	1272.15	1.08950	0.1997
44.09	14.5276	0.94874	1281.70	1.10713	0.1821
29.39	22.1749	0.96544	1291.43	1.13081	0.1641
14.70	45.1353	0.98254	1301.31	1.16916	0.1457
11.76	56.6180	0.98601	1303.31	1.18113	0.1420
8.82	75.7569	0.98948	1305.31	1.19638	0.1383
5.88	114.0364	0.99298	1307.31	1.21761	0.1345
2.94	228.8781	0.99648	1309.32	1.25346	0.1308
		(at 2100° F.)			
200.72	2.8962	0.82747	1222.05	1.01427	0.2907
191.05	3.0691	0.83460	1226.33	1.01802	0.2843
176.35	3.3685	0.84555	1232.93	1.02402	0.2746
161.66	3.7232	0.85671	1239.65	1.03041	0.2647
146.96	4.1500	0.86812	1246.53	1.03727	0.2545
132.26	4.6733	0.87982	1253.56	1.04469	0.2438
117.57	5.3293	0.89184	1260.76	1.05281	0.2327
102.87	6.1750	0.90419	1268.14	1.06178	0.2210
88.18	7.3053	0.91689	1275.68	1.07186	0.2088
73.48	8.8911	0.92993	1283.38	1.08342	0.1962
58.78	11.2738	0.94332	1291.24	1.09711	0.1830
44.09	15.2503	0.95703	1299.25	1.11413	0.1695
29.39	23.2108	0.97106	1307.39	1.13717	0.1556
14.70	47.1065	0.98539	1315.66	1.17488	0.1415
11.76	59.0565	0.98829	1317.32	1.18671	0.1386
8.82	78.9739	0.99120	1319.00	1.20183	0.1357
5.88	118.8100	0.99412	1320.67	1.22294	0.1328
2.94	238.3209	0.99706	1322.35	1.25865	0.1299
		(at 2200° F.)			
258.93	2.2962	0.81446	1227.64	1.00579	0.2883
249.83	2.3966	0.82022	1230.99	1.00853	0.2832
235.14	2.5752	0.82948	1236.43	1.01312	0.2752
220.44	2.7775	0.83875	1241.91	1.01791	0.2675
205.74	3.0090	0.84807	1247.45	1.02295	0.2599
191.05	3.2765	0.85751	1253.08	1.02828	0.2522
176.35	3.5892	0.86709	1258.80	1.03394	0.2444
161.66	3.9596	0.87686	1264.64	1.03998	0.2364
146.96	4.4051	0.88685	1270.59	1.04649	0.2280
132.26	4.9509	0.89704	1276.66	1.05355	0.2194
117.57	5.6346	0.90748	1282.86	1.06128	0.2104
102.87	6.5154	0.91818	1289.19	1.06985	0.2011
88.18	7.6920	0.92913	1295.64	1.07951	0.1914
73.48	9.3417	0.94033	1302.22	1.09064	0.1814
58.78	11.8194	0.95179	1308.91	1.10388	0.1710
44.09	15.9531	0.96350	1315.71	1.12044	0.1604
29.39	24.2262	0.97544	1322.63	1.14302	0.1495
14.70	49.0571	0.98761	1329.64	1.18024	0.1384
11.76	61.4741	0.99007	1331.05	1.19198	0.1361
8.82	82.1699	0.99254	1332.47	1.20700	0.1339
5.88	123.5626	0.99502	1333.89	1.22800	0.1316
2.94	247.7427	0.99751	1335.31	1.26362	0.1293
		(at 2300° F.)			
327.66	1.8487	0.79977	1232.76	0.99802	0.2905
323.31	1.8796	0.80232	1234.18	0.99908	0.2878
308.62	1.9899	0.81078	1238.94	1.00271	0.2796
293.92	2.1107	0.81905	1243.64	1.00644	0.2722
279.22	2.2438	0.82718	1248.32	1.01028	0.2654
264.53	2.3916	0.83525	1253.00	1.01426	0.2589
249.83	2.5567	0.84330	1257.70	1.01840	0.2527
235.14	2.7425	0.85137	1262.45	1.02272	0.2465
220.44	2.9532	0.85950	1267.24	1.02727	0.2404
205.74	3.1944	0.86771	1272.10	1.03205	0.2343
191.05	3.4732	0.87604	1277.03	1.03712	0.2280
176.35	3.7990	0.88451	1282.05	1.04252	0.2216
161.66	4.1847	0.89312	1287.15	1.04830	0.2150
146.96	4.6484	0.90191	1292.35	1.05453	0.2082
132.26	5.2162	0.91087	1297.64	1.06130	0.2011
117.57	5.9272	0.92001	1303.03	1.06873	0.1938
102.87	6.8427	0.92935	1308.52	1.07699	0.1863
88.18	8.0650	0.93888	1314.10	1.08633	0.1784

(*Continued on page 467*)

Table III. Thermodynamic Properties of Potassium Vapor in the Superheat[a] Region (*Continued*)

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

p	v_g	z	h^g	s^g	c_p^g
		(at 2300° F. cont.)			
73.48	9.7782	0.94860	1319.77	1.09712	0.1704
58.78	12.3505	0.95852	1325.54	1.11002	0.1621
44.09	16.6409	0.96862	1331.40	1.12623	0.1536
29.39	25.2264	0.97890	1337.33	1.14845	0.1450
14.70	50.9920	0.98937	1343.35	1.18530	0.1361
11.76	63.8762	0.99148	1344.57	1.19697	0.1343
8.82	85.3503	0.99360	1345.78	1.21191	0.1325
5.88	128.2995	0.99573	1347.00	1.23284	0.1307
2.94	257.1488	0.99786	1348.22	1.26839	0.1289
		(at 2400° F.)			
407.60	1.5055	0.78181	1236.71	0.99066	0.3013
396.79	1.5590	0.78815	1240.07	0.99291	0.2933
382.10	1.6359	0.79639	1244.50	0.99597	0.2838
367.40	1.7182	0.80429	1248.81	0.99907	0.2756
352.70	1.8068	0.81191	1253.02	1.00222	0.2683
338.01	1.9025	0.81932	1257.16	1.00543	0.2618
323.31	2.0066	0.82659	1261.26	1.00873	0.2558
308.62	2.1204	0.83376	1265.34	1.01211	0.2502
293.92	2.2454	0.84086	1269.42	1.01562	0.2449
279.22	2.3835	0.84793	1273.51	1.01925	0.2398
264.53	2.5369	0.85501	1277.63	1.02302	0.2348
249.83	2.7084	0.86211	1281.77	1.02697	0.2298
235.14	2.9016	0.86927	1285.97	1.03110	0.2249
220.44	3.1208	0.87649	1290.21	1.03544	0.2199
205.74	3.3716	0.88380	1294.51	1.04003	0.2148
191.05	3.6614	0.89122	1298.87	1.04490	0.2096
176.35	4.0000	0.89874	1303.30	1.05009	0.2042
161.66	4.4008	0.90640	1307.80	1.05565	0.1988
146.96	4.8824	0.91418	1312.38	1.06166	0.1931
132.26	5.4720	0.92211	1317.03	1.06820	0.1873
117.57	6.2098	0.93018	1321.75	1.07539	0.1813
102.87	7.1596	0.93839	1326.55	1.08341	0.1751
88.18	8.4273	0.94676	1331.43	1.09250	0.1687
73.48	10.2037	0.95527	1336.38	1.10304	0.1622
58.78	12.8703	0.96393	1341.40	1.11567	0.1554
44.09	17.3172	0.97274	1346.49	1.13161	0.1486
29.39	26.2148	0.98169	1351.65	1.15354	0.1416
14.70	52.9150	0.99078	1356.87	1.19011	0.1344
11.76	66.2662	0.99261	1357.93	1.20172	0.1330
8.82	88.5186	0.99445	1358.98	1.21661	0.1315
		(at 2400° F. cont.)			
5.88	133.0243	0.99629	1360.04	1.23748	0.1301
2.94	266.5427	0.99814	1361.10	1.27297	0.1286
		(at 2500° F.)			
499.30	1.2328	0.75775	1238.19	0.98323	0.3312
484.97	1.2850	0.76719	1242.94	0.98596	0.3145
470.27	1.3406	0.77612	1247.49	0.98870	0.3006
455.58	1.3987	0.78444	1251.80	0.99142	0.2893
440.88	1.4598	0.79229	1255.92	0.99412	0.2797
426.18	1.5244	0.79975	1259.88	0.99683	0.2714
411.49	1.5929	0.80690	1263.73	0.99957	0.2642
396.79	1.6661	0.81381	1267.49	1.00233	0.2578
382.10	1.7444	0.82052	1271.18	1.00515	0.2520
367.40	1.8287	0.82708	1274.83	1.00802	0.2467
352.70	1.9197	0.83353	1278.44	1.01096	0.2418
338.01	2.0185	0.83989	1282.04	1.01399	0.2372
323.31	2.1261	0.84620	1285.63	1.01710	0.2328
308.62	2.2438	0.85247	1289.23	1.02033	0.2285
293.92	2.3734	0.85874	1292.84	1.02367	0.2244
279.22	2.5165	0.86502	1296.47	1.02714	0.2203
264.53	2.6757	0.87133	1300.13	1.03076	0.2163
249.83	2.8538	0.87768	1303.83	1.03455	0.2122
235.14	3.0543	0.88409	1307.57	1.03853	0.2081
220.44	3.2818	0.89057	1311.36	1.04272	0.2039
205.74	3.5421	0.89713	1315.19	1.04714	0.1996
191.05	3.8428	0.90377	1319.08	1.05185	0.1953
176.35	4.1940	0.91051	1323.02	1.05687	0.1908
161.66	4.6097	0.91734	1327.02	1.06226	0.1862
146.96	5.1090	0.92429	1331.08	1.06809	0.1815
132.26	5.7200	0.93134	1335.20	1.07445	0.1766
117.57	6.4846	0.93851	1339.37	1.08145	0.1716
102.87	7.4684	0.94580	1343.61	1.08927	0.1665
88.18	8.7813	0.95319	1347.91	1.09816	0.1613
73.48	10.6207	0.96071	1352.26	1.10850	0.1559
58.78	13.3813	0.96834	1356.68	1.12092	0.1504
44.09	17.9845	0.97609	1361.14	1.13664	0.1447
29.39	27.1940	0.98395	1365.67	1.15836	0.1390
14.70	54.8286	0.99192	1370.25	1.19471	0.1332
11.76	68.6468	0.99353	1371.17	1.20627	0.1320
8.82	91.6776	0.99514	1372.09	1.22112	0.1308
5.88	137.7397	0.99676	1373.02	1.24194	0.1296
2.94	275.9272	0.99838	1373.94	1.27739	0.1284

[a] Values are given to more significant figures than the data warrant in order to retain precision in differences.

dimeric vapors. If the NRL data are taken arbitrarily as a reference and the property changes from p_s to 0.2 atm. compared at each temperature, the enthalpy changes reported by Walling are 17 to 95% high and the entropy changes are 2 to 14% high. Similarly, the enthalpy changes reported by Weatherford are 28 to 40% low, and the entropy changes are 5 to 8% low. Specific heats and specific volumes of potassium vapor were tabulated by Walling, and these values also are in considerable disagreement with those of NRL.

In the existing compilations of properties for potassium, the reported values can be no better than the accuracy of the assumptions which made the calculations possible. The properties reported in this paper are based on measured compressibilities. They have been evaluated by several tests for internal consistency, and it is believed that they will be satisfactory for any type of calculation now required for the design of systems using potassium as heat-transfer or working fluid.

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NOMENCLATURE

B = second virial coefficient, cu. ft./ mole
C = third virial coefficient, $(\text{cu. ft.})^2/(\text{mole})^2$
D = fourth virial coefficient, $(\text{cu. ft.})^3/(\text{mole})^3$
c_p = specific heat at constant pressure, B.t.u./lb.-° F.
f = free energy, B.t.u./lb.
h = enthalpy per unit mass, B.t.u./lb.
Δh = enthalpy change per unit mass, B.t.u./lb.
Δh_v = enthalpy change upon vaporization of a unit mass of equilibrium vapor, B.t.u./lb.

ΔH_v = enthalpy change upon vaporization of a mole of equilibrium vapor, B.t.u./lb.-mole
J = any unit conversion
M_1 = molecular weight of monomeric species
p = absolute pressure, p.s.i.
Q = a defined function, $[(z-1)\tilde{V} - B]\tilde{V}$
R = gas constant
s = entropy per unit mass, B.t.u./lb.-° F.
Δs_v = entropy change upon vaporization of a unit mass of equilibrium vapor, B.t.u./lb.-° F.
T = absolute temperature, ° R.
t = temperature, ° F.
$\tilde{V}$ = molal volume (per formula weight of monomer), cu. ft./lb.-mole
v = specific volume, cu. ft./lb.
z = compressibility factor, $p\tilde{V}/RT$

Subscripts

i = quantity at any state
o = quantity at 0° R.
p = constant pressure change
s = quantity at saturation

Superscripts

g = quantity in gas state
l = quantity in liquid state
$^\circ$ = standard state, 1 atm. for gas

LITERATURE CITED

(1) Deem, H.W., Eldridge, E.A., Lucks, C.F., "The Specific Heat from 0° to 1150° C. and Heat of Fusion of Potassium," **Batt-4673-T2,** (August 1962).
(2) Douglas, T.B., Ball, A.F., Ginnings, D.C., Davis, W.D. *J. Am. Chem. Soc.* 74, 2472 (1952).
(3) Evans, W.H., Jacobson, R., Munson, T.R., Wagman, D.D., *J. Res. Natl. Bur. Std.* **55**, 83 (1955).
(4) Herzberg, G., "Molecular Spectra and Molecular Structure, I. Spectra of Diatomic Molecules," Van Nostrand New York, 1950.
(5) Hicks, W.T., *J. Chem. Phys.* **38**, 1873 (1963).
(6) Hirschfelder, J.O. Curtiss, C.F., Bird, R.B., "Molecular Theory of Gases and Liquids," Wiley, New York, 1954.
(7) Hirschfelder, J.O., McClure, F.T., Weeks, I.F., *J. Chem. Phys.* **10**, 201 (1942).
(8) Makansi, M.M., Madsen, M., Selke, W.A., Bonilla, C.F., *J. Phys. Chem.* **60**, 128 (1956).
(9) Stone, J.P., Ewing, C.T., Spann, J.R., Steinkuller, E.W., Williams, D.D., Miller, R.R., J. CHEM. ENG. DATA 11, 309 (1966).
(10) *Ibid.*, p. 315.
(11) *Ibid.*, p. 320.
(12) Walker, B.E., Ewing, C.T., Miller, R.R., *Rev. Sci. Instr.* **33**, 1029 (1962).
(13) Walker, B.E., Grand, J.A., Miller, R.R., *J. Phys. Chem.* **60**, 231 (1956).
(14) Walling, J.F., Lemmon, A.W., Jr., "Experimental *P-V-T* Properties of Potassium to 1150° C." **BATT-4673-T4** (April 1963).
(15) Walling, J.F., Nuzum, H.K., and Lemmon, A.W., Jr., "Vapor Pressure and Heat of Vaporization of Potassium from 480 to 1150° C." **BATT-4673-T3** (April 1963).
(16) Weatherford, W.D., Jr., Tyler, J.C., Ku, P.M., "Properties of Inorganic Energy-Conversion and Heat-Transfer Fluids for Space Application," WADD Tech. Rept. **61-96** (November 1961).
(17) Woolley, H.W., *J. Chem. Phys.* 21, 236 (1953).

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High-Temperature Properties of Sodium

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A virial equation of state for sodium with coefficients through the fourth virial is derived from *PVT* data covering a temperature range from 1750° to 2525° F. Exact thermodynamic relations involving the virial and vapor-pressure equations are used to generate saturation and superheat properties of the vapor. Values of enthalpy, entropy, specific heat, and specific volume are tabulated for some 140 selected vapor states in the temperature range from 1650° to 2550° F. and in the pressure range from 2.9 to 358.7 p.s.i.a. The thermal properties for a somewhat greater temperature range from 1400° to 2500° F. are presented as a Mollier chart.

THE existing thermodynamic properties of alkali metal vapors have for the most part been obtained by estimating imperfections from spectroscopic data. The properties so obtained are of questionable accuracy, and there is a need for an increased reliability for the evaluation of the metal vapors as working fluids in turbines and other power cycles. To meet this need, reliable thermodynamic properties of sodium, potassium, and cesium are being generated from sets of experimentally determined properties—pressure-volume-temperature, vapor pressure, and liquid density. These properties for all three metals have been reported by Stone *et al.* (*10, 11, 12*), and those for potassium have been reduced thermodynamically to yield a consistent body of vapor properties—enthalpy, entropy, specific heat, and specific volume (*3*). This article describes a similar reduction of the measured properties of sodium.

TREATMENT OF *PVT* DATA AND THE VIRIAL EQUATION OF STATE

The major imperfections in sodium vapor at the temperatures and pressures involved in this study stem from the existence of molecular species with two or more atoms (*5*). These species are present in such abundance that an equation of state of the quasichemical type (involving equilibrium constants) could have been used to represent the *PVT* data. However, the virial equation was preferred over the quasichemical types since the thermodynamic relationships based on it are believed to be better established.

The *PVT* data of Stone and coworkers (*10*) were fitted by the graphical method described for potassium (*3*) and the resulting virial equation of state is