

HEAT OF EVAPORATION AND CRITICAL PARAMETERS OF THE ALKALI METALS

L. D. Volyak

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An expression containing one universal constant is proposed for the dependence of the heat of evaporation of the alkali metals on the specific volume of the liquid phase. The critical parameters of the alkali metals are refined.

As shown in [1], over the entire region of the liquid state the specific heat of evaporation can be described with a high degree of accuracy by the equation

$$r = B [e^{-c_1 v'} - e^{-c_1 v_* - c_2 (v'' - v')}] \tag{1}$$

Here, B, c<sub>1</sub>, and c<sub>2</sub> are constants, v' and v'' are the specific volumes of the phases, and v\* is the critical specific volume. Equation (1) satisfies limiting conditions at the critical point.

The second term in (1) is important only on a temperature interval of about 30° adjacent to the critical point. Therefore, if we exclude this region, we can employ the simpler relation

$$r = B e^{-c v'} \tag{2}$$

In [1] Eqs. (1) and (2) were verified for a considerable number of nonmetallic liquids. It is of interest to apply the same equations to the alkali metals. For this purpose we plotted graphs of the function lg r = f(v'), which proved to be linear and enabled us to determine the constants B and c, whose values relative to the equation

$$r = B 10^{-c v'} \tag{3}$$

are presented in Table 1.

Table 1

	B, 10 <sup>3</sup> J/kg	c, kg/m <sup>3</sup>	Bc, 10 <sup>6</sup> J/m <sup>3</sup>	D <sub>0</sub> <sup>0</sup> , 10 <sup>3</sup> kJ/mole	ΔH <sub>01</sub> <sup>0</sup> , 10 <sup>3</sup> kJ/mole	p*, 10 <sup>6</sup> N/m <sup>2</sup>	ρ*, kg/m <sup>3</sup>
Li	41120	129.7	5332	106.8	159.3	1000	120
Na	8340	242.8	2025	70.68	107.9	365	206
K	4030	212.0	854.4	53.80	90.16	179	194
Rb	1909	465.0	887.6	50.87	82.65	124	346
Cs	1153	564.1	650.4	47.10	78.58	102	428

In these calculations the values of v' for Li, Na, and K were taken from [2], those for Rb and Cs from [3]. Values of the heat of evaporation of the alkali metals were calculated thermodynamically by the method described in [4], using values of the dissociation energy D<sub>0</sub><sup>0</sup> and heat of sublimation ΔH<sub>01</sub><sup>0</sup> taken from [5] for Li and from [6] for Na and K; for Rb and Cs these values were calculated on the basis of the experimental data of [7] for the saturation vapor pressure. The values of D<sub>0</sub><sup>0</sup> and ΔH<sub>01</sub><sup>0</sup> are presented in Table 1. By way of example, Table 2 gives a comparison of the values of r calculated for K from the data of [4] and from Eq. (3).

Table 2

T° K	[4]	(3)	T° K	[4]	(3)
400	2193	2209	1000	4942	4945
500	2162	2170	1100	1893	1893
600	2127	2130	1200	1846	1839
700	2087	2084	1300	1801	1785
800	2041	2041	1400	1750	1740
900	1992	1994			

As distinct from nonmetallic liquids, for the alkali metals it proved possible to establish the content of the coefficients B and c. Table 1 shows that the product Bc decreases monotonically from Li to Cs (K is an exception).

But the critical pressure also decreases (its approximate values according to the data of [8] are presented in Table 1). It may be assumed that the ratio  $Bc/p_*$  is constant for all the alkali metals, i. e.,

$$Bc = 55.11p_*, [p_*] = N/m^2. \quad (4)$$

Using the values of  $Bc$ , with the aid of (4) we can refine the approximate values of  $p_*$  obtained in [8]; these refined values are presented in Table 3. Contrary to expectation the critical pressure of K proved to be less than that of Rb.

Table 3

	$T_*, \text{ }^\circ K$	$p_*,$ $10^5 \text{ N/m}^2$	$\rho_*,$ $\text{kg/m}^3$	$K$	$\Delta H^\circ,$ $10^3 \text{ J/mole}$
Li	3800	968	98.5	4.63	156
Na	2500	368	184.5	4.52	104.4
K	2070	155	161	4.56	86.5
Rb	1900	161	353	4.05	79.0
Cs	1790	118	428	4.07	74.8
Hg	1763	1510	4700	2.28	62.2

The critical parameters of the alkali metals have not yet been measured experimentally; calculation gives very different values [8, 9]. The uncertainty of the values of the critical density  $\rho_*$  is particularly great; however, a comparison of the value of the coefficient  $c$  in Eq. (3) with the values of  $\rho_*$  obtained by various investigators [10, 11] shows that the coefficient  $c$  increases with increase in the critical density of the alkali metal.

Clearly, it is desirable to give preference to [11] in which the values of  $\rho_*$  for Na, K, Rb, and Cs were established as a result of extrapolation to the critical point of the experimental values of the density of both phases. Using the values of  $\rho_*$  from [11] (Table 1), we obtain

$$c = 1.316 \rho_*. \quad (5)$$

Using the values of  $c$  from Table 1 and Eq. (5), we can refine the values of  $\rho_*$  given in [11]. These refined values are presented in Table 3. They coincide with the values of  $\rho_*$  calculated in [12] from the surface tension.

From (4) and (5) it follows that

$$B = 41.84 p_* v_* \text{ J/kg} \quad (6)$$

and the specific heat of evaporation can be represented by a universal function of the reduced volume  $\varphi = v^l/v_*$  of the liquid phase

$$r = 41.84 p_* v_* 10^{-1.316 \varphi}. \quad (7)$$

In [8] values of the heat of evaporation of the alkali metals were used to calculate their critical temperature  $T_*$ . These values of  $T_*$ , corrected slightly for the more accurate values of the heat of evaporation used in this study, are presented in Table 3.

Kopp [13] recently found that the critical temperature of metals, determined by calculation (only the value of  $T_*$  for mercury was established experimentally), is approximately proportional to the molar heat of evaporation  $\Delta H$

$$T_* = 0.0268 \Delta H, \quad [\Delta H] = \text{J/mole}$$

Kopp did not indicate the temperature to which the heat of evaporation must be referred; it proved possible to establish that for alkali metals the relation

$$T_* = 0.024 \Delta H^\circ \quad (8)$$

is closely satisfied. Here,  $\Delta H^\circ$  is the molar heat of evaporation at the melting point in J/mole, calculated from the formula  $\Delta H^\circ = \Delta H_{01}^\circ + \Delta(H^\circ - H_0^\circ)$ . Values of the function  $H^\circ - H_0^\circ$  for alkali metals were taken from [5].

As Table 3 shows, mercury does not satisfy relation (8), hence Kopp's proposed universal (for metals) expression of the type  $T_* \sim \Delta H$  is not applicable.

Using (6), for the critical coefficient of the alkali metals  $K = RT_*/p_* v_*$  we obtain an expression containing only

one critical parameter  $T_*$  and the relatively reliably established coefficient B of Eq. (2):

$$K = 41.84RT_*/AB$$

(A is the atomic weight). Table 3 shows that with respect to the value of the critical coefficient the alkali metals fall into two distinct groups: Li, Na, and K, for which on average  $K = 4.57$ , and Rb and Cs, for which on average  $K = 4.06$ . The difference of 11% can not easily be attributed to the error in determining the values of B and  $T_*$  for Rb and Cs, but there is some confirmation for it in [11]. The value of K for mercury is much less than for the alkali metals, to which it is undoubtedly thermodynamically dissimilar. In the mercury calculations the necessary data were taken from [10, 14, 15].

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