

## Thermodynamic Characteristics of Vaporization of Alkali Metals

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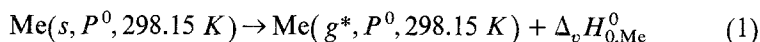
The saturation vapor of an alkali metal is treated as a monatomic particle real gas whose volumetric behavior is described by a truncated form of virial equation. The condensed state-vapor equilibrium constant, equal to the saturation fugacity for Li, Na, K, and Cs, is determined through evaluation of the second virial coefficient's temperature dependence. The third and the second law values of standard enthalpy of vaporization at the reference temperature 298 K for the same metals are determined. The applied procedure for evaluation of the second virial coefficient's temperature dependence produced small deviations for the resulting second law values and gave mean values in good agreement with literature data, especially with those of the JANAF Tables.

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**KEY WORDS:** alkali metals; enthalpy of vaporization; saturated vapor; vaporization; virial coefficient.

### 1. INTRODUCTION

The saturated vapor of an alkali metal represents a mixture of various species; first of all, of monatomic and diatomic molecules. The determination of standard enthalpy of vaporization of these metals, with  $\Delta_v H_{0,Me}^0$  as an enthalpy of vaporization for the process<sup>2</sup>



is based on the third law expression

$$\Delta_v H_{0,Me}^0 = T\Delta_v \Phi - RT \ln K_v \quad (2)$$

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<sup>2</sup>For an explanation of symbols, see nomenclature at end of article.

where  $K$  is the equilibrium constant corresponding to the evaporation process given by Eq. (1) and  $\Phi = -(G_T^0 - H_0^0)/T$  is the free energy function.

The vapor phase can be treated for low temperatures (and low vapor pressures) as an ideal gas. First calculations [1] start from this point of view and, neglecting dimer presence in the saturated vapor, apply the mentioned procedure with

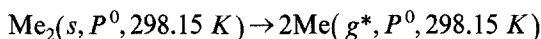
$$K_v = p^s \quad (3)$$

using values of the free energy function for the monatomic species.

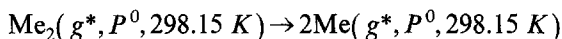
For low temperatures, Evans et al. [2] treat the alkali metal saturated vapor as an ideal gas mixture of atoms and diatomic molecules. They calculate  $\Delta_v H_{0,Me}^0$  in the following way:

$$\Delta_v H_{0,Me}^0 = \frac{1}{2} \Delta_v H_{0,Me_2}^0 + \frac{1}{2} \Delta_d H_{0,Me_2}^0 \quad (4)$$

where  $\Delta_v H_{0,Me_2}^0$ , the enthalpy for the process



is to be determined using Eq. (2), taking for  $K_v$  the experimental value of  $\text{Me}_2$  species equilibrium partial pressure and for  $\Phi(g^*)$  the value of the free energy function for the  $\text{Me}_2$  ideal gas state; for  $\Delta_d H_{0,Me_2}^0$ , the enthalpy of the dimer dissociation process,



the spectroscopic value is to be used.

The procedure of treating the vapor phase as a monatomic real gas, when

$$K_v = f^s \quad (5)$$

takes into account the presence of different species in the vapor [4–6].

In the determination of  $\Delta_v H_{0,Me}^0$  by the third law expression, Eq. (2), as carried out by Hultgren et al. [1], the volumetric behavior of the vapor is described by the equation of state

$$PV = RT + \frac{bP}{T^m} + \frac{cP^2}{T^3} \quad (6)$$

They optimize the values of  $b$ ,  $c$ , and  $m$  parameters using relations deduced from Eqs. (2), (5), and (6). The parameter optimization procedure gives to

Eq. (6) a completely empirical character. Calculation of  $\Delta_v H_{0,Me}^0$  by the second law expression using for  $K_v$

$$K_v = P^s$$

or

$$K_v = P^s \exp\left(\frac{aP^s}{RT^{m+1}} + \frac{cP^{s^2}}{RT^3}\right)$$

gives different results for  $\Delta_v H_{0,Me}^0$  with very high deviation from mean values.

Ewing et al. [3] have established the temperature dependence of  $B$ ,  $C$ , and  $D$  virial coefficients for Na, K, and Cs from vapor phase  $P$ - $V$ - $T$  experimental data in the 20–3500 kPa pressure range and 950–1650 K temperature range. From those, as well as from the experimentally established temperature dependence of vapor pressure, Ewing et al. have determined  $\Delta_v H_{0,Me}^0$  of alkali metals on the basis of Eqs. (2) and (5). These corrected calculations, based on experimental results, have shortcoming, in that the pressure and temperature ranges of virial coefficients and those of  $\Delta_v H_{0,Me}^0$  calculations do not coincide. For the  $\Delta_v H_{0,Me}^0$  calculation for Li, Na, K, and Cs, we have given a procedure that comprises, at the same time, an evaluation of the second virial coefficient's temperature dependence, in the temperature range just below the normal boiling point.

## 2. CALCULATION OF THERMODYNAMIC PROPERTIES

We consider an alkali metal saturated vapor as a monatomic real gas. Its volumetric behavior we describe by a virial equation truncated at the second term. Hill [4], Kilpatrick [5], and Sinanoglu and Pitzer [6] by theoretical considerations show that, at elevated temperatures due to pronounced dissociation and association, for a  $P$ - $V$ - $T$ -relation description of a gas containing multiatomic besides monatomic particles, the virial coefficient formalism of a pure gas is more appropriate than an equation of state for mixtures. On the basis of theoretical work of O'Connell and Prausnitz [7] and that of Woolley [8], we represent the temperature dependence of  $B$  by the relation

$$B = -aT \exp\left(\frac{b}{T}\right) \quad (7)$$

In the calculations, we used an experimentally established vapor pressure

temperature dependence

$$\ln P^s = \alpha + \frac{\beta}{T} + \gamma \ln T \quad (8)$$

with  $\alpha$ ,  $\beta$ , and  $\gamma$  parameters' values taken for Na, K, and Cs from ref. [9] and for Li from the Kubaschewski tables [10]. Calculation of  $\Delta_v H_{0,Me}^0$  has been performed by the third and the second law expressions

$$\Delta_v H_0^0(\text{III}) = T\Delta\Phi - RT \ln P^s - BP^s \quad (9)$$

$$\Delta_v H_0^0(\text{II}) = -\Delta(H_T^0 - H_0^0) + RT^2 \frac{d \ln P^s}{dT} + T^2 \frac{d}{dT} \left( \frac{BP^s}{T} \right) \quad (10)$$

From the last four equations we deduced the expression

$$B = T - \frac{\Delta(H_T^0 - H_0^0) + T\Delta\Phi - RT \ln P - R(\beta + \gamma T)}{|(1 + \gamma)T + \beta - b|P} \quad (11)$$

Parameters  $a$  and  $b$  for Li, Na, K, and Cs have been optimized on the basis of the last equation, as well as from the equation

$$\ln \frac{|B|}{T} = \ln a + \frac{b}{T} \quad (12)$$

applying the combined methods of simple iterations and of linear regression. First, for input value of  $b_0$ , through Eq. (11) at seven temperatures in a range 500 K below the normal boiling point,  $B_0$  values are calculated. After that, from the set of  $B_0$  values obtained, using the linear regression method,  $a_1$  and  $b_1$  values are deduced. From a new set of  $B(B_1)$  values calculated by Eq. (11), using  $a_1$  and  $b_1$  values, a linear regression method yielded next  $a_2$  and  $b_2$  values, etc. The iterations were performed up to  $\delta b_i = (b_{i+1} - b_i)/b_i \leq 10^{-5}$ . The correlation coefficient of the linear regression achieved a value of 0.999.

Using optimized  $a$  and  $b$  parameters, optimized values (Table I) of  $\Delta_v H_{0,Me}^0$  as third and second law values for the mentioned seven temperatures of all cited alkali metals are calculated. In  $a$  and  $b$  parameter optimization as well as in  $\Delta_v H_0^0$  calculations, we used free energy function and  $(H_T^0 - H_0^0)$  values for the condensed state and monatomic particles' ideal gas state from the JANAF tables [11]. With optimized values for the  $a$  and  $b$  parameters, through the expression for the saturation fugacity,

$$\ln f^s = \alpha + \beta + \gamma \ln T - \frac{aT}{R} \exp\left(\alpha + \frac{\beta + b}{T}\right)$$

Table I. Values of the Parameters  $a$  and  $b$  and Mean Values of  $\Delta_v H_{0,Me}^0$ 

Metal	$a \times 10^8$ ( $\text{m}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ )	$b \times 10^{-3}$ (K)	$\Delta_v H_{0,Me}^0$ ( $\text{J} \cdot \text{mol}^{-1}$ )
Li	0.02164	17.239	$160,558 \pm 30$
Na	0.17220	10.523	$107,877 \pm 50$
K	2.96293	5.201	$89,484 \pm 188$
Cs	1.48163	6.204	$76,876 \pm 167$

deduced from the aforementioned description of the volumetric behavior of the saturated vapor of the alkali metal during calculations of  $\Delta_v H_0^0(\text{III})$ , we calculated  $f^s$ , i.e., the alkali metal condensed state-vapor equilibrium constant for the cited temperatures.

### 3. DISCUSSION

In  $\Delta_v H_{0,Me}^0$  mean values are presented in Table I with maximal deviation of third and second law values.  $\Delta_v H_{0,Me}^0$  maximal possible error (for Li, Na, and K, it was  $\leq 500 \text{ J} \cdot \text{mol}^{-1}$  and for Cs  $\leq 15000 \text{ J} \cdot \text{mol}^{-1}$ ), deduced from errors of  $\Phi$ , ( $H_T^0 - H_0^0$ ), and  $P^s$ , in all cases was higher than the deviation of calculated results from their mean value.

Results obtained for  $\Delta_v H_{0,Me}^0$  for all metals are in good agreement with values cited in the literature (Table II) if we take into account the dispersion of the separate values as well as the error of determination. The dispersion of calculated values in our case is smallest in spite of the fact that we take both second and third law values. It is normal because of successful  $a$  and  $b$  parameter optimization based on two exact thermodynamic relations. Subsequent calculations of  $\Delta_v H_{0,Me}^0$  have been performed by the same relations. At the same time the mentioned fact confirms the validity of the accepted form of the second virial coefficient's temperature dependence.

Table II. Values of  $\Delta_v H_{0,Me}^0$  ( $\text{J} \cdot \text{mol}^{-1}$ ) for  $T_0 = 298.15 \text{ K}$ 

Ref.	Li	Na	K	Cs
Hultgren et al. [1]	$161,940 \pm 1,670$	$108,240 \pm 630$	$89,660 \pm 210$	$78,170 \pm 290$
Evans et al. [2]	$160,940 \pm 410$	$108,260 \pm 210$	$89,980 \pm 340$	
Ewing et al. [3]		107,200	90,540	76,360
JANAF Tables [11]	$160,780 \pm 1,670$	107,810	$89,200 \pm 840$	76,690
This work	$160,558 \pm 30$	$107,877 \pm 50$	$89,484 \pm 188$	$76,876 \pm 167$

Table III. Enthalpies of Dissociation ( $\text{kJ} \cdot \text{mol}^{-1}$ ) and  $bR$  Values of Alkali Metals

Metal	Temperature range	$bR$	$\Delta_d H_{0, \text{Me}_2}^0$	$\Delta_d H_{T, \text{Me}_2}^0$	$\Delta_d H_{0, \text{Me}_2^+}^0$
	(K)				
Li	1300–1800	143.40	99.04	209.80	157.81 $\pm$ 8.4
Na	1000–1400	87.53	73.26 $\pm$ 4.1	77.26 $\pm$ 4.1	94.19 $\pm$ 2.1
K	900–1300	43.26	53.58 $\pm$ 4.2	56.76 $\pm$ 4.2	87.91 $\pm$ 25.11
Cs	800–1200	51.60	38.01	40.62	46.05 $\pm$ 8.37

Only for *K* we obtained a  $b$  parameter value which is a linear function ( $bR \sim \Delta_d H_{0, \text{Me}_2}^0$ ) of the dimer dissociation standard enthalpy (Table III) as is anticipated by the Woolley [8] and O'Connell–Prausnitz [7] models in consideration of atomic and diatomic molecular gas mixture. The  $bR$  values for Li, Na, and Cs are higher than the corresponding  $\Delta_d H_{0, \text{Me}_2}^0$  and in all cases are close to the corresponding ionized dimer dissociation standard enthalpy  $\Delta_d H_{0, \text{Me}_2^+}^0$  (Table III). This is difficult to explain unless as a coincidence. Nevertheless, we find it interesting to mention that applying the just described procedure and using the free energy function, the  $(H_T^0 - H_0^0)$  values [1, 2, 11] and vapor pressure temperature dependence [9, 10, 12] from different sources for Na, we obtained  $b$  values such that  $bR$  is always close to  $\Delta_d H_{0, \text{Me}_2^+}^0$  [13] (Table IV).

Values of subexponential parameters of the virial coefficient temperature dependence for Na, K, and Cs vapors presented by Ewing et al. [3] correspond to the Woolley model ( $bR \sim \Delta_d H_{T, \text{Me}_2}^0$ ) if one assumes that  $\Delta_d H_{T, \text{Me}_2}^0$  is not temperature dependent. However, even if Ewing et al. determine the virial coefficient's temperature dependence from  $P, V, T$  experimental measurements, during the inference of the virial coefficient's temperature dependence, they prescribe parameter values that are subexponential (proportional to  $\Delta_d H_{0, \text{Me}_2}^0$ ). This is a reason why their third and fourth virial coefficients' temperature dependences do not correspond to the Woolley model [8].

Table IV. Calculated Values of  $\Delta_v H_{0, \text{Me}}^0$  and  $b$  for Sodium

Reduced functions ref.	Vapor pressure ref.	$\Delta_v H_{0, \text{Na}}^0$ ( $\text{kJ} \cdot \text{mol}^{-1}$ )	$b$ (K)	$bR$ ( $\text{kJ} \cdot \text{mol}^{-1}$ )
[1]	[12]	108.70	10.454	86.96
[1]	[10]	109.06	11.770	97.90
[2]	[12]	108.20	10.600	88.17
[11]	[9]	107.88	10.523	87.53

#### 4. CONCLUSIONS

Alkali metal vapor is treated as a gas for which the volumetric behavior is described by a virial equation truncated to the second term. Use of an exponential in Woolley's relation is anticipated for the second virial coefficient's temperature dependence. The third and second law value of  $\Delta_v H_{0,Me}^0$  for Li, Na, K, and Cs are calculated from the vapor pressure, free energy function, and  $(H_T^0 - H_0^0)$  values at temperatures below the normal boiling point, using the author's procedure by which at the same time the second virial coefficient temperature dependence and the vapor-liquid equilibrium constant equal to saturated fugacity have been evaluated.

Results obtained for  $\Delta_v H_0^0$  with small deviations from mean values are in good agreement with literature data, especially with those of JANAF tables. The value obtained for the  $b$  subexponential parameter in the case of K corresponds to the theoretical statements: the  $bR$  value is close to the  $K_2$  dissociation enthalpy. In the case of Li, Na, and Cs, the  $bR$  values are higher than  $\Delta_d H_{0,Me_2}^0$  and approach  $\Delta_d H_{0,ME_2^+}^0$ .

#### NOMENCLATURE

$P$	pressure
$V$	volume
$T$	temperature
$G$	Gibbs function
$H$	enthalpy
$\Phi = -(G_T^0 - H_0^0)/T$	the free energy function
$H_T^0 - H_0^0$	reduced enthalpy
$B, C, D$	virial coefficients
$\alpha, \beta, \gamma$	vapor pressure temperature dependence coefficients
$a, b$	parameters of virial coefficient temperature dependence
$K_v$	equilibrium constant
$f$	fugacity
Me	metal

#### SUPERSCRIPTS

- 0 standard state
- \* ideal gas state
- $s$  saturation state

**SUBSCRIPTS**

- 0 reference temperature
- v* vaporization
- d* dissociation

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