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Evaluation of P-V-T-Composition Characteristics of Carbon Saturated Vapor

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Volumetric behavior of carbon saturated vapor, in the temperature range 2500–3200 K, is described by two approaches: by the truncated form of the virial equation for the real monatomic gas and by the ideal gas equation of state for the mixture of present C_i species. The literature data for C_i partial pressure and $\Delta_v H^0_{0,C_i}$ are analyzed through the comparison of the vapor pressure values deduced by the first approach with the data. New data for p_3 and $\Delta_v H^0_{0,C_3}$ are then evaluated. The values for carbon vapor pressure and saturated vapor molar volume calculated by two different approaches show remarkable agreement.

KEY WORDS: carbon; enthalpy of vaporization; vapor pressure; virial coefficient.

1. INTRODUCTION

Carbon saturated vapor represents a mixture of molecular species C_i, with a different number of C atoms, $i = 1, 2, 3, \ldots$. Up to 4000 K, the contribution by the species above C_5 is quite negligible [1]. Due to pronounced dissociation and association, the virial coefficient formalism of a pure monatomic gas can be more appropriate for description of the volumetric behavior of such a system [2, 3] than the equation of state for the ideal gas mixture. We have described in two ways the volumetric behavior of carbon saturated vapor: by the truncated form of the virial equation of state (first approach) and by the ideal gas equation of state for the mixture of present molecular species (C_1 to C_5) (second approach).

In the first approach [4], which has not been applied earlier to the carbon saturated vapor, we evaluated the equations representing depen-

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dence of the total carbon vapor pressure and to the second virial coefficient on temperature[2]

$$\ln \frac{P}{P^0} = 887.502 - \frac{229{,}701}{T} + 0.021521T - 110.54 \ln T \qquad (1)$$

$$B = -8.239 \times 10^{-12} \exp \frac{73{,}484}{T} \qquad (2)$$

where T is in K and B is in $\mathrm{m}^3 \cdot \mathrm{mol}^{-1}$. These equations have been established for the temperature range 2500–3200 K, through an original numerical iterative procedure [4], based on the third and second law expressions for standard enthalpy of vaporization, $\Delta_v H^0_{0,\mathrm{C}_1}$, developed by using the anticipated general expressions for $P = f(T)$ (equation of the Rankin–Kirchoff type) and for $B = f(T)$ (Woolley's exponential form [5]).

In our previous paper [4] we stated that, first, the use of Eqs. (1) and (2) in the calculation of the standard enthalpy of vaporization gives third and second law values that are close to each other, both in good agreement with the literature data [6–10]. Second, the obtained value of the $B = f(T)$ subexponential parameter, $b = 73{,}484$, corresponds to the anticipated Woolley's theoretical model [5], the bR product being approximately equal to the standard enthalpy of carbon dimer dissociation ($\Delta_d H^0_{0,\mathrm{C}_2}$). Third, the values of carbon vapor pressure in the temperature range 2500–3200 K, calculated by Eq. (1), are lower then those based on the reported literature data (Fig. 1). Fourth, the established carbon vapor pressure temperature dependence (Eq. 1) gives for the sublimation temperature of carbon a value $T_s = 4080$ K, which is close to the experimental one [6, 7] (Fig. 1).

The last established fact suggests that applicability of the evaluated carbon vapor pressure temperature dependence (Eq. 1) can be extended up to 4100 K, while all the cited statements lead to the conviction that the applied approach gives reliable results. In order to further check the validity of this approach, as well as of the obtained results, especially for the carbon vapor pressure, we have computed, in this work, relevant thermodynamic parameters of the carbon saturated vapor as an ideal gas mixture, using the ideal gas equation of state. Finally, we compared the results obtained by the two different approaches.

In this work we have also analyzed the literature values of the properties (partial pressure, enthalpy of vaporization) of molecular species

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[2] For an explanation of symbols, see nomenclature at the end of the article; standard pressure $P^0 = 101{,}325$ Pa.

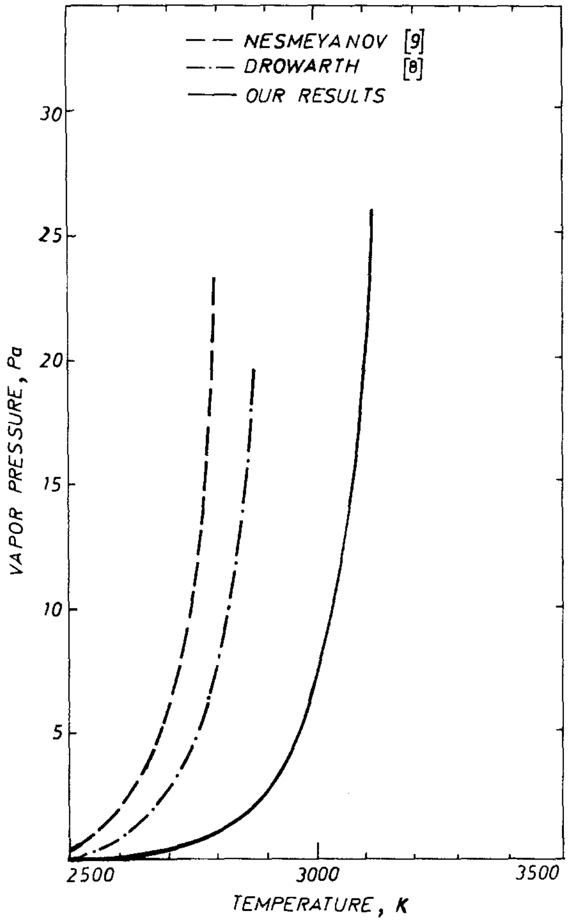

Fig. 1. Vapor pressure of carbon as a function of temperature.

present in the carbon saturated vapor and recalculated them for the C_3 species. Since in the second approach the volumetric behavior of carbon saturated vapor is described by the ideal gas equation of state, the carbon vapor pressure is equated to the sum of equilibrium partial pressures of all the present molecular species,

$$P = \sum_{i=1}^{5} p_i \tag{3}$$

and the molar volume (volume per gram-atom) of saturated vapor is given by the expression

$$v(II) = RT \Big/ \sum_{i=1}^{5} ip_i \tag{4}$$

while according to the first approach, the same quantity is equal to

$$v(I) = \frac{RT}{P} + B \tag{5}$$

2. CALCULATION OF THERMODYNAMIC PROPERTIES

In the presentation of the carbon vapor pressure as a sum of partial pressure, we started from the assumption that the values calculated by Eq. (1) are real and absolutely reliable. By comparing these values with the literature (lit) data [7–12], it can be said that they are (a) lower than the sum of partial pressure values,

$$P(\text{Eq. 1}) < \sum_{i=1}^{5} p_i(\text{lit}) \tag{6}$$

(b) higher than each particular partial pressure value for the C_1, C_2, C_4, and C_5 species,

$$P(\text{Eq. 1}) > p_i(\text{lit}) \qquad i = 1, 2, 4, 5 \tag{7}$$

(c) lower than the literature values for the partial pressure of the C_3 species,

$$P(\text{Eq. 1}) < p_3(\text{lit}) \tag{8}$$

and (d) higher than the value of the partial pressure sum, excluding p_2 and p_3,

$$P(\text{Eq. 1}) > \sum_{\substack{i=1 \\ i \neq 2,3}}^{5} p_i(\text{lit}) \tag{9}$$

On this basis, we have pointed out that it is necessary to select among the published literature data the appropriate values for both p_2 and $\Delta_v H^0_{0,C_2}$ and to recalculate p_3 and $\Delta_v H^0_{0,C_3}$ values. We accepted as reliable the C_1, C_4, and C_5 partial pressure values, which can be computed from the JANAF tables [10] and satisfy the test of thermodynamic consistency, which implies that for temperature $T = 2600$, 2700, and 2800 K, the following identities are fulfilled:

$$\ln p_i(T) = \ln K_i - \frac{d_i}{T} \tag{10.1}$$

$$K_i = \exp \frac{\Delta_v S^0_{2700,\,C_i}}{R} \tag{10.2}$$

$$d_i = \frac{\Delta_v H^0_{2700,C_i}}{R} \tag{10.3}$$

$$\Delta_v H^0_{0,C_i} = \Delta_v H^0_{2700,C_i} - \Delta_v(H^0_{2700} - H^0_0)C_i \tag{10.4}$$

$$p_i = P^0 \exp\left(\frac{\Delta_v H^0_{0,C_i} - T\Delta_v \Phi_{C_i}}{RT} \right) \tag{10.5}$$

Here we have taken as appropriate p_2 values that we have obtained through Eqs. (10.1)–(10.5), using $(H^0_T - H^0_0)$ and free energy function values for graphite and C_2 from the JANAF tables [10], and the value $\Delta_v H^0_{2700,C_2} = 861.62\ \mathrm{kJ \cdot mol^{-1}}$ obtained by Zavitasanos in the experiments based on the combined Knudsen effusion and mass-spectrometry methods [11]. Among Zavitasanos's results, we have selected as the most appropriate the $\Delta_v H^0_{T,C_2}$ value deduced from experiments with a pyrolitic graphite crucible, performed in a narrow temperature range (2700–2900 K). We have not accepted p_2 and $\Delta_v H^0_{0,C_2}$ values given in other publications [6–10], where the partial pressures sum, excluding p_3, is higher then P values from Eq. (1):

$$P(\text{Eq. }1) < \sum_{\substack{i=1 \\ i\neq 3}}^{5} p_i(\text{lit}) \tag{11}$$

By subtracting the appropriate p_1, p_2, p_4, and p_5 values from the vapor pressure values computed by Eq. (1), we have estimated C_3 single partial pressure values for given temperatures:

$$p_3 = P(\text{Eq. }1) - \sum_{\substack{i=1 \\ i\neq 3}}^{5} p_i \tag{12}$$

For temperatures of 2600, 2700, and 2800 K, these values are used as the starting p_3 values in the iterative procedure applied to evaluate both $\Delta_v H^0_{0,C_3}$

and p_3 values. The simple iterative procedure based on Eqs. (10.1)–(10.5) includes the following steps.

First, we get K_3 and d_3 values from the p_3 starting values, obtained by Eq. (12), by applying the linear regression method by the expression (10.1):

$$\ln p_3 = \ln K_3 - \frac{d_3}{T} \tag{13}$$

Second, we calculate $\Delta_v H^0_{0,\mathrm{C}_3}$ with the obtained d_3 value, using $(H^0_T - H^0_0)$ and free energy function data from ref. 13. Finally, we calculate $p_3(T)$ set values by Eq. (10.5). The iteration was stopped when the correlation coefficient in Eq. (10.1) reached the value 0.99988. The calculated p_3 values at 2600, 2700, and 2800 K gave for the C_3 vaporization standard enthalpy second and third law values of 917.528 and 917.494 kJ · mol^{-1}, respectively (Table I). The values of p_3 in the temperature range 2500–3200 K were calculated using the mean of these values. Carbon vapor pressure values were then obtained by Eq. (3) on the basis of p_3 obtained above (Table II).

Calculations of the carbon vapor molar volume by Eq. (5) were extended from the saturation state [4] to the superheated state near the saturated region. With the values of v thus obtained, isobars for $v = f(T)_P$, showing the condensation boundary for precipitation of graphite, were constructed (Fig. 2). In the second approach we computed saturated vapor molar volume only for the temperature range 2500–3200 K through Eq. (4),

Table I. Thermodynamic Consistency Test Data

	Molecular species/ thermodynamic functions [ref.]				
	C_1 [10]	C_2 [10]	$C_3{}^a$ [13]	C_4 [10]	C_5 [10]
d_i (Eq. 10.1)(K^{-1})	8.5766E04	1.0357E05	1.0603E05	1.1399E05	1.1491E05
K_i (Eq. 10.1)	1.3958E08	5.4480E09	3.0780E10	1.6563E10	4.7611E10
$\Delta_v S^0_{2700}$ (Eq. 10.1) (J · mol^{-1} · K^{-1})	653.12	780.78	839.43	819.50	856.26
$\Delta_v S^0_{2700}$ (table value) (J · mol^{-1} · K^{-1})	652.96	780.82	840.86	819.50	856.98
$\Delta_v H^0_{2700}$ (Eq. 10.3) (kJ · mol^{-1})	713.841	861.623	882.020	948.271	955.761
$\Delta_v H^0_{298}$(II) (kJ · mol^{-1})	715.968	876.050	917.528	971.063	979.236
$\Delta_v H^0_{298}$(III) (kJ · mol^{-1})	715.813	876.046	917.494	971.180	979.629

[a] Data for C_3 species are computed through the described numerical procedure.

Table II. Molecular Species Partial Pressure and Carbon Vapor Pressure (P/P^0 Dimensionless Values) for Various Temperatures (in K)

	2500	2600	2700	2800	2900	3000	3100	3200
p_1 [10]	1.7610E-07	6.5897E-07	2.2359E-06	6.9527E-06	1.9977E-05	5.3468E-05	1.3419E-04	3.1770E-04
p_2 [11]	5.5272E-09	2.7274E-08	1.1926E-07	4.9635E-07	1.6767E-06	5.4966E-06	1.6673E-05	4.7074E-05
p_3 (Eq. 12)	1.3483E-08	6.5212E-08	2.9459E-07	9.9800E-07	3.5824E-06	1.2409E-05	4.1540E-05	1.3392E-04
p_3 (Eq. 10)	1.1745E-08	6.0012E-08	2.7179E-07	1.1047E-06	4.0767E-06	1.3790E-05	4.3133E-05	1.2557E-04
p_4 [10]	2.6007E-09	1.5031E-09	7.6389E-09	3.4458E-08	1.4029E-07	5.1742E-07	1.7518E-05	5.4754E-04
p_5 [10]	5.1637E-09	3.0433E-09	1.5641E-08	7.1513E-08	2.9371E-07	1.0954E-06	3.7438E-04	1.1810E-05
p (Eq. 1)	1.9589E-07	7.5600E-07	2.6731E-06	8.5260E-06	2.5670E-05	7.2980E-05	1.9790E-04	5.1580E-04
p (Eq. 3)	1.9408E-07	7.5080E-07	2.6503E-06	8.6328E-06	2.6171E-05	7.4171E-05	1.9866E-04	5.0352E-04
$\delta(\%)^a$	0.87	0.69	0.86	1.25	1.93	1.89	0.85	1.62

[a] $\delta = \left(1 - \frac{P\ (\text{Eq. }3)}{P\ (\text{Eq. }1)}\right) \times 100\%.$

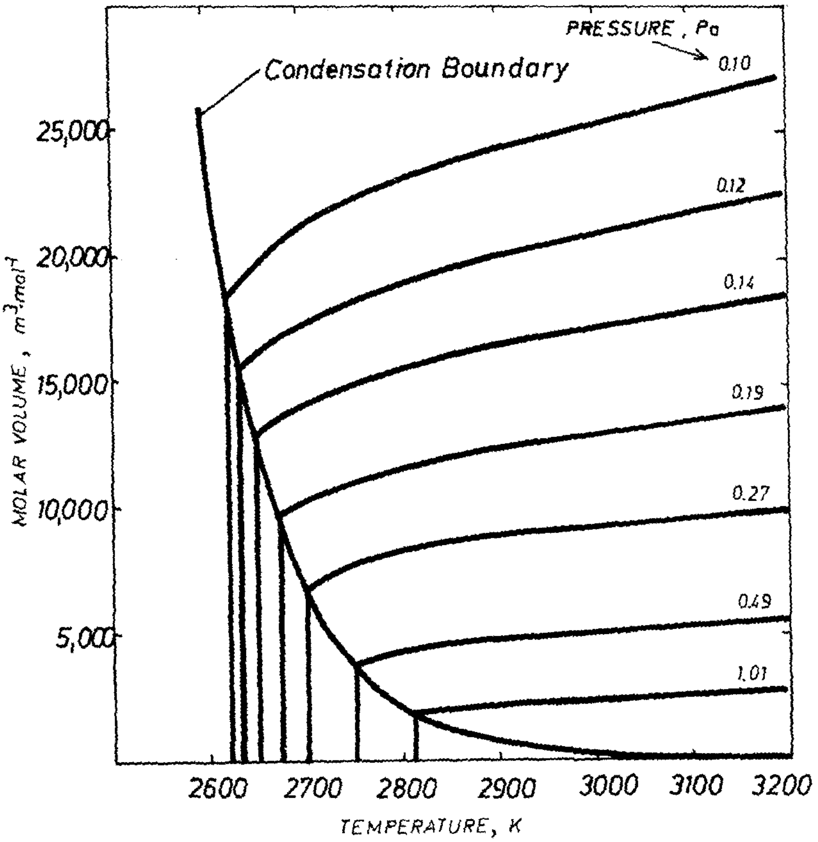

Fig. 2. Molar volume of carbon as a function of temperature.

Table III. Carbon Saturated Vapor Molar Volume (m^3mol^{-1})

Temperature (K)	$v(I)$	$v(II)_1$[a]	$v(II)_2$[a]	δ_1[b] (%)	δ_2[b] (%)
2500	9.2834E05	8.8840E05	9.9889E05	4.50	3.15
2600	2.4220E05	2.2954E05	2.3378E05	4.38	3.48
2700	6.8281E05	6.3971E04	6.5277E04	6.31	4.40
2800	2.1213E04	2.0196E04	1.9645E04	4.79	7.98
2900	6.8650E03	6.4195E03	5.3363E03	6.49	7.70
3000	2.3030E03	2.2564E03	2.1740E03	2.02	5.60
3100	7.8270E02	8.0113E02	7.8934E02	2.35	0.85
3200	2.7550E02	2.9387E02	3.0234E02	6.67	9.75

[a] In the calculation of $v(II)_1$ the p_3 value computed by Eq. (12) is used, while in the calculation of $v(II)_2$ the p_3 value from the described numerical procedure is used.

[b] $\delta = \left(1 - \frac{v(II)}{v(I)}\right) \times 100\%$.

using as p_3 values first the values obtained by Eq. (12) and then values calculated in this work (Table III).

3. DISCUSSION

The carbon vapor pressure calculated by Eq. (3) as a sum of partial pressures, using the p_3 values evaluated by the described procedure and appropriate p_1, p_2, p_4, and p_5 values (Fig. 3), has a value equal to the carbon vapor pressure computed by Eq. (1), i.e., deviations of the two computed values do not exceed 2.0% (Table II). The obtained condensation boundary for precipitation of graphite is shifted towards lower temperatures and higher molar volume in comparison with the results in ref. 6 (Fig. 2). This, however, as expected since our carbon vapor pressure values are higher. The condensation boundary calculated by Eq. (4) (second approach), using p_3 values obtained by Eq. (12), as well as those evaluated by the applied procedure, coincides with the evaluated through Eq. (5) (first approach). Deviations of v(II) from v(I) are less than 7% when p_3 values from Eq. (12) are used. In the case when v(II) is calculated with p_3 deduced by the applied numerical procedure, these deviations do not exceed 10% (Table III).

The established agreement between the values for the carbon vapor pressure, as well as for the saturated molar volume, calculated by two approaches, therefore, proves the validity of the procedure used in the first approach. These agreements can also be used as a proof of reliability of the evaluated equations expressing dependence of the second virial coefficient and carbon vapor pressure on temperature, as well as of reliability of all the obtained results.

Unreliability of the literature values for both $\Delta_v H^0_{0,C_3}$ and p_3 has long been an unsolved problem [6]. The recalculation of the C_3 thermodynamic functions [13, 14] and the reevaluation of p_3 and $\Delta_v H^0_{0,C_3}$ values performed by Meyer and Lynch [12] on the basis of new estimated values of conversion factors (of ion intensity to partial pressure) are contributions to the solution of this problem, but not a definite answer. Zavitasanos, who presents different $\Delta_v H^0_{0,C_3}$ third and second law values, accepts the possibility that the second law values are influenced by the temperature dependence of the ionization cross-section. One of the reasons for uncertainty of $\Delta_v H^0_{0,C_3}$ published results is the fact that $\Delta_v H^0_{T,C_3}$ and $\Delta_v G_{T,C_3}$ are highly dependent on temperature (more than the corresponding thermodynamic properties of other C_i species [10, 13]). Therefore we selected as appropriate a $\Delta_v H^0_{2700,C_2}$ value obtained from measurements in a narrow temperature range, and we performed $\Delta_v H^0_{0,C_3}$ optimization over a temperature range of 200 K.

The literature data for p_3, as well as those for $\Delta_v H^0_{0,C_3}$, remain doubtful

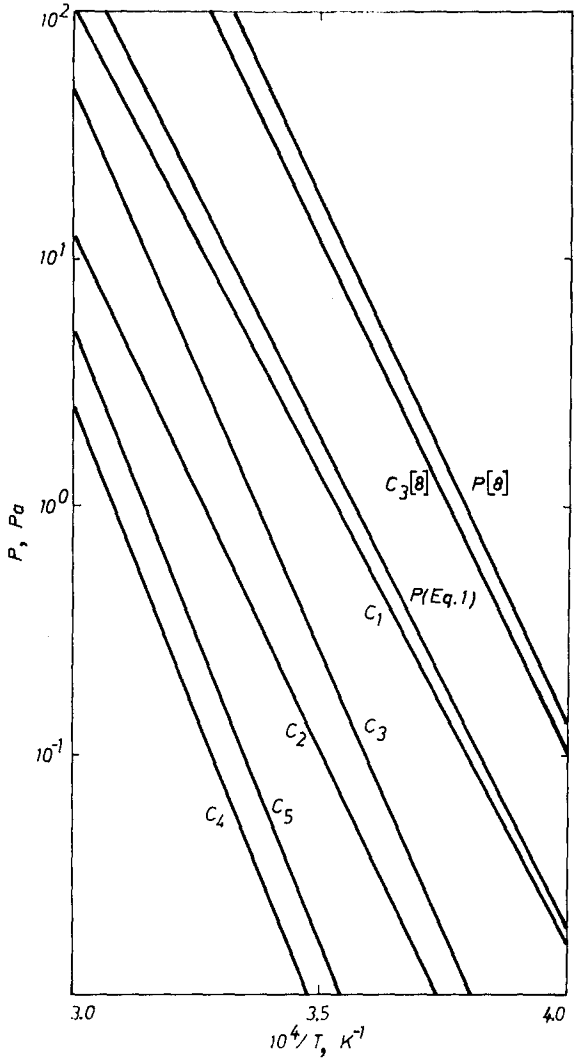

Fig. 3. Arrhenius plot of the appropriate partial pressure of C_i species.

after comparison of the carbon vapor pressure values derived by the first approach with the literature data for the partial pressure of molecular species present in the carbon saturated vapor. The procedure used in our calculations of new values of $\Delta_v H^0_{0,C_3}$ and p_3 is indeed intermediary, but ensures thermodynamic consistency of all the obtained thermodynamic data for C_3 (Table I), i.e., identity of $\Delta_v S^0_T$ values deduced from p_3

evaluated values and those obtained from S_T^0 table data [13], as well as full agreement between $\Delta_v H^0_{0,C_3}$ third and second law values.

4. CONCLUSIONS

Temperature dependence of carbon vapor pressure and the second virial coefficient, deduced by the approach treating carbon saturated vapor as monatomic particles in real gas, are used for calculation of carbon vapor pressure and vapor molar volume values in the temperature range 2500–3200 K. In order to check the validity of this approach and of the obtained results, the same thermodynamic characteristics of the carbon saturated vapor have also been determined by the approach in which volumetric behavior is described by the equation of state for the ideal gas mixture.

Viewing the literature data for C_3 species partial pressure and standard vaporization enthalpy as doubtful, a new value for $\Delta_v H^0_{0,C_3} = 917.11\ \mathrm{kJ \cdot mol^{-1}}$ has been derived. With p_3 values calculated by using this value together with the anticipated partial pressure values for other C_i species, the carbon vapor pressure is calculated as a sum of partial pressures. Thus obtained values are equal to that of the carbon vapor pressure evaluated by the first approach described above. Molar volumes of the carbon saturated vapor computed by the two applied approaches agree within the limits of 10%. The established agreement of the carbon vapor pressure and saturated vapor molar volume values is a proof of the validity of the procedure used in the first approach, as well as of the reliability of the obtained results.

NOMENCLATURE

P	pressure, vapor pressure
p_i	partial pressure
V	volume
v	molar volume
T	temperature
G	Gibbs function
H	enthalpy
S	entropy
R	gas constant
B	second virial coefficient
b	subexponential parameter of virial coefficient temperature dependence
Φ	free energy function, $-(G_T^0 - H_0^0)/T$

Superscript

0	standard state

Subscripts

d dissociation
i molecular species
0 reference temperature
v vaporization

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