Pressure-Volume-Temperature Relationships for Cesium Vapor

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A quasichemical equation of state for cesium vapor is derived from PVT information covering a temperature range from 1300° to 3385° F. The implications of the equation are discussed and it is used with the rectilinear diameter law and the Clapeyron equation to compute saturation properties to 3150° F.

Metallic fluids, and in particular the alkali metals, are of great interest in many space and nuclear power programs where coolants and working fluids are required at high temperatures. Thermophysical properties of saturated and superheated phases are needed for the design and development of these power systems.

In the recent past, PVT (*24*), vapor pressure (*25*), and liquid density (*26*) of sodium, potassium, and cesium were measured at the Naval Research Laboratory to temperatures approaching 2400° F. The objective of the present program was to extend this work to the critical state for cesium by additional PVT measurements at higher temperatures. This article follows the reporting of saturation pressures (*4*).

METHODS

The basic measuring apparatus was a simple constant volume chamber fabricated from T111 alloy (90% tantalum, 8% tungsten, 2% hafnium) with a flexible diaphragm of the same material for sensing pressures. At each equilibrium temperature, the pressure of argon external to the measurement chamber was adjusted so that the diaphragm was just making or breaking electrical contact with an insulated probe. Under these conditions, the pressure of inert gas (except for a small deflection correction which was always below 0.1 psi) was equal to the pressure of cesium vapor and was observed externally at room temperature with Bourdon-tube gages. Since the same technique was used for the saturation studies (*4*), details of the apparatus and the tungsten resistance furnace will not be repeated.

The PVT determinations required the measurement of four parameters: pressure (to 125 atm), temperature (to 3400° F), volume, and weight. It was necessary at these extreme conditions to determine all four parameters with unusual accuracy in order to permit the generation of reliable properties.

Five 12-in. precision gages were used with ranges of 50, 150, 500, 1500, and 2500 psi. They were calibrated, *in situ*, with dead weight piston gages at Eastern Standards Laboratory. The sensitivities of the tantalum alloy diaphragms were such that they would generally make and break electrical contact without any readable change of the pressure gage. This implies a sensitivity of less than 0.1 psi, which was shown experimentally to remain unchanged for temperature cycles from room temperature to 3400° F.

Equilibrium temperatures were measured with thermocouples of tungsten-3% rhenium and tungsten-25% rhenium. All of the measurement thermocouples were cut from 50-ft rolls of the two tungsten-rhenium alloys and indirectly calibrated by the direct calibration (to 3450° F) of couples from the ends of the rolls at the National Bureau of Standards. Calibration differences for the two couples ranged from 0.00 mV at 1450° F-0.02 mV at 3450° F. The stability and reliability of these couple systems were further established by simultaneous measurements of temperature with an automatic optical pyrometer (Leeds & Northrup 8642) sighted on a black-body hole. This pyrometer and the glass window in the optical path were also calibrated at NBS. The average difference in temperature as measured by the two methods was less than 0.1%.

The cesium used for the tests was a high purity grade from MSA Research Corp. Clean transfer operations and precision weighing techniques (*25*) in an inert gas handling box required an additional distillation of the metal from a glass retort into tantalum alloy ampuls. A typical spectrographic analysis of the alkali metal after one distillation is presented in Table I. Volatile and nonvolatile impurities are present in concentrations too low to produce a measurable vapor-pressure change.

The volume of each apparatus was obtained by precise dimensioning of the chamber with appropriate corrections applied for the thermal expansion of the tantalum alloy. Dimensional changes after firing were low and were within the expected error of the dimensioning technique.

EXPERIMENTAL RESULTS

Superheat properties for cesium are reported in Table II. For each experimental condition, equilibrium was assured by taking multiple readings of temperature and pressure at 5- to 10-min intervals until successive readings showed a temperature drift of less than 0.2° F/min. The temperature gradient along the axis of the measurement chamber was controlled within 2° F/cm, usually within 1° F.

The results reported in Table II were obtained from two experimental runs with temperature ranges covering both saturation and superheat states. The first run has

Table I. Typical Spectrographic Analysis of Cesium

Metal impurity	Ppm
Na	100[a]
K	<10[a]
Rb	<500[a]
Ca	1-10
B	<1
Si	10-100
Mg	<1
Li, Al, Mn, Fe, Cu, Ba, Sr	ND[b]

[a] Used standard samples for comparison; figures should be quantitative. [b] Not detected.

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Table II. PVT Properties of Cesium

Temp, °F	Pressure, atm	Sp vol, ft^3/lb
3385.0	124.13	0.0705
2813.9	64.957	0.1738
2926.8	69.482	0.1741
2994.3	72.026	0.1743
3076.2	75.068	0.1745
3209.9	79.893	0.1748
3310.9	83.751	0.1750
3443.5	88.317	0.1753
3184.5	79.273	0.1747
2970.0	71.394	0.1742

only one recorded point in the superheat range. Another point, at 3182.5°F and 106.11 atm, was initially recorded as superheat data, but subsequent analysis has shown that this point is near the intersection of the saturation and superheat curves where pressures are known to be severely depressed (*4*, *24*). Consequently, this point is not recorded in Table II and is given no weight in the development of the equation of state.

EQUATION OF STATE

Program termination prevented the accumulation of additional high temperature information, and it is impossible to develop an equation of state solely from the data in Table II. Extensive *PVT* information for cesium has been measured and published (*24*) in the temperature range from the normal boiling point to about 2350°F. This permitted us to fit the lower temperature information with a quasichemical equation of state and to use the high temperature information to test the extension of the equation. This is equivalent to fitting a composite of the information with an equation of state.

Cesium vapor is known from spectroscopic studies (*13*) to be partially associated into molecules, and there are two general theories dealing with association and gas imperfections. One is discussed by Hirschfelder *et al.* (*15*) and fundamentally assumes that all imperfections may be regarded as the association of perfect gas atoms to form perfect gas assemblies of two or more atoms. The other theory, illustrated in the work of Vukalovich *et al.* (*28*), also assumes that the atoms in the gas combine to form stable molecules but that the interacting particles and molecules must be treated as imperfect gases.

Existing information on metal vapor systems does not permit a definition of the physical state of cesium vapor. It was necessary, therefore, to test the fit of the composite PVT information to several quasichemical models. In a previous paper (*8*) by the present authors, quasichemical equations of state were developed for sodium and potassium from PVT information by assuming that all imperfections could be incorporated into association equilibria involving ideal dimers and tetramers. An analysis of the available cesium data at that time indicated that the PVT information could not be fitted successfully to the ideal-gas model. After subsequent testing with the composite data, it became even more obvious that it would be necessary to consider interaction imperfections in order to obtain a fit with an equation of state.

Vukalovich *et al.* (*28*) have derived a practical working relationship for imperfect systems with one or more association equilibria. This relationship (Equation 1) is a form of the van der Waals equation:

$$(P + A_1/\tilde{V}^2)(\tilde{V} - B_1) = (M_1/M_a)RT \qquad (1)$$

The internal pressure term $(A_1/\tilde{V}^2)$ and the volume coefficient (B_1) were derived using additive laws and the only coefficients remaining in the final form are those for the monomeric gas. The average molecular weight of the gas, M_a, is regulated by the effect of temperature and pressure on the association equilibria.

Three different equations of state were selected for study as representing the three most likely vapor models—an imperfect mixture of monomeric and dimeric species; an imperfect mixture of monomeric, dimeric, and trimeric species; and an imperfect mixture of monomeric, dimeric, and tetrameric species. Computer programs were developed to fit and to test the fit of the three quasichemical equations to the composite *PVT* information. It was arbitrarily assumed in each case that both of the van der Waals coefficients would be independent of temperature. For all three models, it was necessary to fix a value for one of the coefficients. The value of B for a material is known to be related to the molal volume of the liquid, and one can obtain a consistent value of the coefficient for cesium either from a correlation of experimental volume coefficients (Figure 1) for nonpolar and weakly polar organic and inorganic fluids at their normal boiling points; or from the relationship (*9*),

$$B_1 = \tilde{V}_{c,1}/3 = \tilde{V}_c/3$$

A value of 1.8245 ft^3/lb-mole was selected from Figure 1 and this is approximately one-third of the value generally estimated for the critical volume of cesium.

For each vapor model, the fitting procedure was as follows. Apparent equilibrium constants of dimerization were computed at a series of values of A_1 for isotherms covering the experimental range, and an iteration procedure was used to select that value for A_1 which gave the most consistent values of k_2, k_2 and k_3, or k_2 and k_4. The methods for generating the higher equilibrium constants from apparent dimerization constants have been fully covered elsewhere (*8*, *17*, *18*).

It was immediately apparent that the experimental information at higher and lower temperatures could not be correlated with an equation of state involving only monomeric and dimeric species. On the other hand, either model with higher molecular weight species could be fitted to the data with low standard deviation. The model with tetramer was arbitrarily selected.

The equation of state for cesium is

$$(P + 10{,}400/\tilde{V}^2)(\tilde{V} - 1.8245) = M_1/M_a RT \qquad (2)$$

$$\log k_2 = -4.0299 + 5261.2/T$$

$$\log k_4 = -10.017 + 10{,}986/T$$

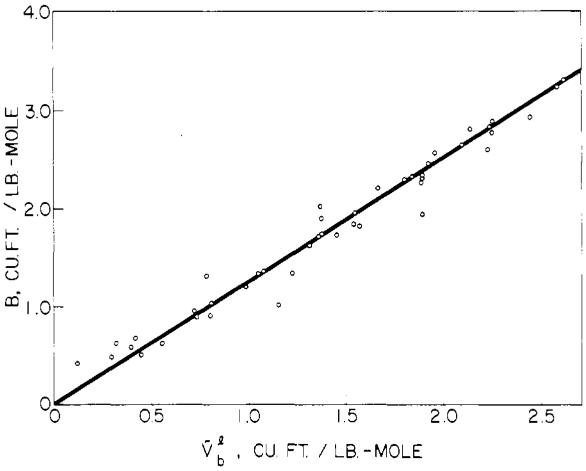

Figure 1. Relationship between the molal volume of the liquid $\tilde{V}_b(l)$ and the van der Waals coefficient *B* for nonpolar and weakly polar organic and inorganic fluids

where

$$k_2 = \frac{N_2}{N_1^2 \,(P + 10{,}400/\tilde{V}^2)}$$

and,

$$k_4 = \frac{N_4}{N_1^4 \,(P + 10{,}400/\tilde{V}^2)^3}$$

The molal volume and information on the apparent composition of the vapor may be obtained from Equation 2 by any one of several iteration schemes (*8*, *27*). If one is primarily interested in obtaining the molal or the specific volume of cesium vapor, the apparent equilibrium constant of dimerization, k_2', can be expressed as a power series (*8*).

$$k_2' = k_2 + 3\,k_4 \left(P + \frac{10{,}400}{\tilde{V}^2}\right)^2 - 2\,k_2k_4 \left(P + \frac{10{,}400}{\tilde{V}^2}\right)^3 \tag{3}$$

in which k_2' is defined as follows:

$$k_2' = \frac{N_2'}{(1 - N_2')^2 \,(P + 10{,}400/\tilde{V}^2)} \tag{4}$$

and

$$M_a = M_1\,(1 + N_2') \tag{5}$$

At a given temperature and pressure state, internally consistent values for the molal volume and molecular weight of the vapor may be computed numerically from Equations 2–5.

At a given temperature, the several equations representing the vapor system may be expressed as a polynomial of the sixth order in $\tilde{V}$. Because of this mathematical complexity, the equation was systematically evaluated at vapor states covering wide ranges of temperature and pressure. The actual volume of cesium vapor is always the largest real root and the equation is not valid in the near critical region. Specific volumes are internally consistent at all temperatures and pressures down to states with a specific volume of 0.086 ft^3/lb, and they are generally consistent down to a value of 0.07 except for a short temperature range near 3300° F. If the equation should be used at temperatures and pressures corresponding to specific volume states down to 0.07, the consistency should be checked by observing the root system as a function of temperature and pressure.

All specific volume data reported by Stone *et al.* (*24*) and in this paper can be calculated from Equation 2 with an average percent deviation of 0.27 and a standard percent deviation of 0.48. The lower temperature data by Stone *et al.* (*24*) can be calculated with an average percent deviation of 0.22 and a standard percent deviation of 0.31, and the high temperature data from this paper with an average percent deviation of 1.1%.

DISCUSSION

The quasichemical equation is not intended to replace the NRL virial equation (*7*) below 2350° F, but to extend saturation and superheat property information to higher temperatures. Even so, specific volumes computed by the virial and the quasichemical equations between 1500° and 2350° F differ at no point by more than 0.8%.

The new equation has been used with the recent vapor-pressure information (*4*), the rectilinear law (*2*), and the Clapeyron equation to extend the saturation properties of cesium to 3150° F (Table III). Although the empirical law of rectilinear diameters has been tested for a large number of organic and inorganic liquids (*11*, *12*) over their full liquid ranges, there is still a question as to the linearity of the rectilinear density of an alkali metal because of the changing composition of the vapor phase. In this connection, consistent liquid and vapor properties have been determined for several of the alkali metals over temperature ranges from their melting points to about 2400° F (*5*, *6*, *7*), and it can be shown (*12*) that deviations from the rectilinear law are very small. Therefore, it is assumed that the changing composition of the vapor is ordered with temperature and that it does not significantly affect the linearity of the rectilinear density.

Table III. Saturation Properties of Cesium

Temp, °F	Density liquid, lb/ft^3	Density vapor, lb/ft^3	Enthalpy of vaporization, Btu/lb
2300	67.310	2.715	157.6
2350	66.012	2.977	154.2
2400	64.697	3.256	150.7
2450	63.363	3.554	147.0
2500	62.009	3.872	143.2
2550	60.633	4.211	139.2
2600	59.233	4.574	135.1
2650	57.808	4.963	130.8
2700	56.355	5.380	126.3
2750	54.869	5.829	121.5
2800	53.346	6.315	116.5
2850	51.780	6.845	111.3
2900	50.163	7.426	105.6
2950	48.480	8.072	99.56
3000	46.711	8.805	92.91
3050	44.816	9.664	85.41
3100	42.704	10.739	76.44
3150	39.966	12.441	63.17

Bonilla and colleagues (*21–23*), by two techniques, have measured an average value of 3231° F for the critical temperature of cesium. With the properties reported in Table III, critical quantities may be predicted from a rectilinear plot by extrapolating properties over a temperature range of less than 100° F. The Columbia value of 3231° F for T_c represents a reasonable extension of the NRL properties. With this value of T_c, the NRL work predicts that P_c is 1700 psia and that d_c is 25.35 lb/ft^3. The value of 1700 psia for P_c is in excellent agreement with the value of 1704 measured by Silver (*23*).

Two other experimental determinations of the specific volume of saturated cesium vapor to temperatures approaching the critical value have been reported (*3*, *16*). In addition, several equations of state (*1*, *7*, *10*, *19*, *20*) have been generated from various vapor-state measurements at lower temperatures. However, it is beyond the scope of this article to make detailed comparisons of Equation 2 with the literature information.

From a theoretical standpoint, it is of interest to compare the empirically derived value of 10,400 for the coefficient A_1 with values for other organic and inorganic fluids which are believed to be nonreactive in the vapor state. An estimate of the interaction coefficient A for a fluid can be obtained from its internal energy of vaporization (*14*). If $A/\tilde{V}^2$ is taken as the internal pressure, and if the work necessary to disperse the liquid into isolated particles is assumed to be equal to the work required to overcome internal pressure, then it follows that

$$A \cong \Delta E_v/[1/\tilde{V}(\mathrm{l}) - 1/\tilde{V}(\mathrm{g})]$$

In Figure 2, the boiling point is used as a rough corresponding state and observed values of A for a large group of nonpolar organic and inorganic fluids are plotted against

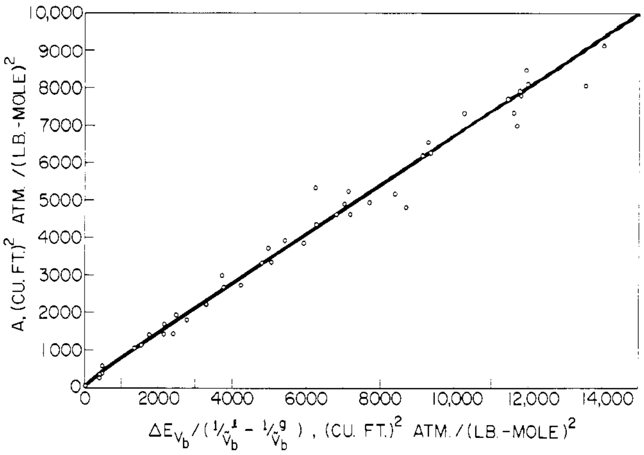

Figure 2. Relationship between the quantity $\Delta E_{V_b}/[1/\tilde{V}_b(l) - 1/\tilde{V}_b(g)]$ and the van der Waals coefficient A for nonpolar and weakly polar organic and inorganic fluids

corresponding computed values. The use of the single value at the normal boiling point is quite satisfactory since the computed values of A for most fluids are practically independent of temperature. The value of

$$\Delta E_v/[1/\tilde{V}(l) - 1/\tilde{V}(g)]$$

at the normal boiling point for monomeric cesium vapor cannot be calculated explicitly, but it can be estimated by correcting ΔE_v and $V(g)$ for the molecular content of the vapor. The value of

$$\Delta E_{v,1}/[1/\tilde{V}(l) - 1/\tilde{V}_1(g)]$$

so obtained is about 14,400 and, from Figure 2, a value of 9600 is predicted for A_1.

The magnitudes of the two coefficients A_1 and B_1 for cesium may be predicted from other inorganic and organic fluids generally believed to be unassociated in the vapor state. This fact, along with the degree of fit obtained for a particular quasichemical equation of state to *PVT* information over extended ranges of temperature and pressure, suggests that the alkali metal vapor is in reality an imperfect mixture of monomeric, dimeric, and a higher molecular weight species.

NOMENCLATURE AND UNITS

A = van der Waals interaction coefficient $[(\text{ft}^3)^2 - \text{atm}]/\text{mole}^2$
B = van der Waals volume coefficient, ft^3/mole
ΔE_v = internal energy change upon vaporization of a mole of equilibrium vapor, btu/mole
(g) = gas state
k = equilibrium constant
(l) = liquid state
M = molecular weight
N = mole fraction
P = absolute pressure, atm
R = gas constant
T = absolute temperature, °R
$\tilde{V}$ = molal volume per formula weight of monomer, ft^3/mole

Subscripts

a = equilibrium molecular mixture
b = normal boiling point
s = saturation
c = critical state
1 = monatomic species
2 = diatomic species
3 = triatomic species
4 = tetratomic species

Superscript

= apparent quantity, when assuming only monatomic and diatomic species

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RECEIVED for review June 10, 1970. Accepted October 7, 1970.