COO-3027-9
Conf-730851--5

PROCEEDINGS OF THE
SIXTH SYMPOSIUM ON THERMOPHYSICAL PROPERTIES - HEAT TRANSFER DIVISION - AMERICAN SOCIETY OF MECHANICAL ENGINEERS - NEW YORK, N.Y.
Atlanta, Ga. August 6 - 8, 1973.

REVISION OF HIGH TEMPERATURE AND CRITICAL PROPERTIES OF CESIUM

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ABSTRACT

The high temperature equilibrium vapor and liquid phase densities of cesium reported previously by this laboratory (O 70) from a "tilting capsule" test have been recalculated with the aid of generalized mathematical relations for the phase densities, instead of a rectilinear diameters line extrapolated from lower temperatures. The critical density and temperature found are 0.420 g/cc and 3686.0 deg R, respectively.

In addition, the earlier high temperature vapor pressure data and critical pressure of cesium by the "pressure tube" method (S 70) were checked with the improved equipment now available, obtaining close reverification. The critical pressure was obtained as 1701.3 psia and the critical temperature by this independent method as 3699.1 deg R.

Using the average critical temperature of 3692.1 ± 8 R, the critical compressibility factor of cesium is calculated as 0.2177.

NOMENCLATURE

A,B,C,D	Constants
C_P	Constant pressure heat capacity cal/g deg C
h	Enthalpy cal/g
ΔH_V	Heat of vaporization K cal/g-atom
K	Dimerization constant
L	Internal length of capsule, cm
M	Mass of cesium charged into tilting capsule, g
P	Vapor pressure, psia
p	Pivot length, cm
R	Gas constant
r	Internal radius of capsule, cm
S	Entropy cal/K g-atom
T	Temperature, deg R
t	Temperature, deg F
W	Weight of empty capsule, g
ΔZ	Change in compressibility factor
$\alpha, \beta, \gamma, \epsilon$	Constants
θ	Tilt angle
ρ	Density, g/cc

Subscripts

C	Critical state
L	Liquid state
P	Constant pressure
R	Reduced property
V	Vapor state

INTRODUCTION

Measurements of the saturated vapor and liquid phase densities at high temperatures were made by Oster and Bonilla using the "tilting capsule" method (O 67, O 70). The method involves hanging a cylindrical capsule that is partially filled with cesium from an off-center transverse knife edge, and measuring the tilt angle at different temperatures. See Fig 1. A complete description of the apparatus and experimental procedure is given elsewhere (O 67, O 70).

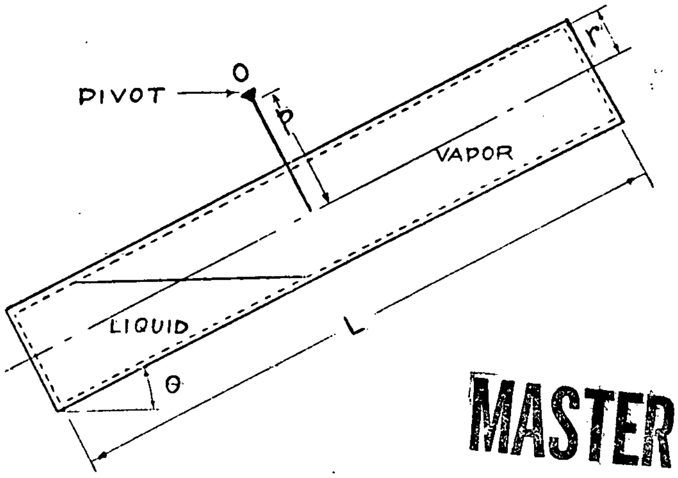

Fig.1 Tilting capsule.

A moment balance around the knife edge gives the following equation for the tilt angle as a function of the liquid and vapor densities:

$$\tan^3 \theta + X \tan^2 \theta + Y = 0 \quad (1)$$

where

$$Y = \frac{\pi r^4(\rho_L-\rho_V)}{8\ p\ (M+W)} \qquad (2)$$

$$\text{and } X = 2Y + \frac{(M-V\rho_V)(M-V\rho_L)}{2\pi r^2\ p(M+W)(\rho_L-\rho_V)} \qquad (3)$$

In these equations, ρ_L and ρ_V are the saturated liquid and vapor densities, M is the mass of cesium charged, and θ is the tilt angle from the horizontal. Also, r is the internal radius of the capsule, V its internal volume and p the pivot length, from the knife edges to the axis, all at test temperature. W, ρ_L and ρ_V include gas buoyancy.

The most significant result is the temperature at which θ just becomes 0, by direct observation or a short extrapolation, as this yields immediately a density figure, for either the liquid or vapor according to whether the average Cs density is greater or less than ρ_c.

If two runs are made at a lower temperature with different masses of Cs in the same capsule, or in two capsules, it is possible to solve the resulting two versions of eq 1 simultaneously for ρ_L and ρ_V at that temperature. If the two runs do not include observations at the same temperature, interpolation is made on one or both graphs of θ vs T. If data are available close to the critical temperature, the critical density can be approximated with relatively small error, and the critical temperature observed very precisely. However, only one run with one capsule was successfully completed, since the second capsule available developed a leak. Accordingly, data or another relation for ρ_L and/or ρ_V as a function of T was required. The simplest, the "law of rectilinear diameters," of Cailletet and Mathias, was accordingly assumed. First, the best straight line obtainable from the many published low temperature Cs density data plus the vertical capsule data of Hochman and Bonilla to 3000 F (H 64) was employed, yielding 0.445 g/cc as ρ_c (O 67). Later the line obtainable from the extrapolation to 3150 F by Ewing et al (E 70) of their Cs PVT data to 2500 F, which fell somewhat lower, was adjudged as probably more accurate in their range, and was employed. The resulting ρ_c for Cs by this approach was 0.406 g/cc (O 70).

NEW ANALYSIS OF DENSITY DATA

Subsequently, improved procedures and data for the analysis of the available tilting capsule run became available, and suggested a new treatment of the run, to obtain more reliable results and a better evaluation of the merit of the method (S 71). First, thermal expansion of the capsule and pivot length was obtained more accurately from recent data (C 66) on Ta-10% W, virtually the same as T-111. Second, the effective pivot length, p, which is crucial in interpreting the tilt angle data, was found more accurately by a calibration procedure than by direct measurement. At the lowest temperatures at which θ was measured ρ_L and ρ_V are well known from other studies. Thus, eq 1 was used in reverse to determine p from the ρ_V and ρ_L data of Ewing et al (E 66a and b).

Third, the previous study assumed the validity of the rectilinear diameters line:

$$1/2\ (\rho_L + \rho_V) = a - bT \qquad (4)$$

at all temperatures up to the critical. This "law" has been widely reported in the literature as valid for many materials. At low temperatures, the liquid density decreases almost linearly with temperature, while the vapor density is almost zero. Thus $(\rho_L + \rho_V)$ must decrease almost linearly with temperature, and even up to $T_R = 0.5$ deviations from the rectilinear diameters line are bound to be small. However, no broad theoretical basis has been found for eq 4, and its validity up to the critical point itself is not universal. Accordingly, for the second relation involving ρ_L and/or ρ_V an established empirical equation for ρ_V as a function of T was used. This method has a feature in that ρ_V does not rise to a substantial fraction of ρ_L until T_R is of the order of 0.95, so that a ρ_V correlation of only moderate % accuracy will suffice for fairly accurate ρ_L values.

Various equations for the vapor and liquid density of cesium have been reported. Hochman and Bonilla (H 64, H 65a, b) report polynomials in T, Ewing et al (E 66a, b) report a polynomial in T for ρ_L and a virial equation for ρ_V, and Miller (M 70) reports equations of the type

$$\rho = \rho_c + \beta(1 - T_R)^{\gamma} \qquad (5)$$

for both liquid and vapor in the critical region. Dillon (D 67) reports ρ_L and ρ_V values for cesium over a wide temperature range but these show considerable scatter. Also, Van der Waals equations of state have been reported for cesium by Ewing (E 71), and by Grosse (G 68), who uses the form developed by Martin (M 67).

At first sight it appears that both ρ_L and ρ_V cannot be determined from the T vs θ data collected in these experiments, since only data from one run are available. However, if correct equation forms for ρ_L and ρ_V are available, it is possible to set up a least squares computational scheme that determines ρ_L and ρ_V as functions of T using a non-linear generalized curve-fitting procedure. Incorporating the linear decrease in ρ_L with rising T at low T, and eq 5 for the critical region, plus an empirical second power correction term, eq 6 was adopted:

$$\rho_L = \rho_c + \alpha_L\ (1 - T_R) + \beta_L\ (1-T_R)^{\gamma_L} + \epsilon_L(1 - T_R)^2 \qquad (6)$$

By analogy, eq 7 was also adopted:

$$\rho_V = \rho_c + \alpha_V (1 - T_R) + \beta_V (1-T_R)^{\gamma_V} + \epsilon_V (1 - T_R)^2 \qquad (7)$$

Differentiating eq 6 or 7:

$$\left(\frac{\partial \rho}{\partial T_R}\right)_{T_R=1} = - \frac{\beta \gamma}{(1-T_R)^{1-\gamma}} \qquad (8)$$

so that if β_L is positive and β_V negative

$$\left(\frac{d\rho_L}{d T_R}\right)_{T_R=1} = -\infty \qquad (9)$$

$$\left(\frac{d\rho_V}{d T_R}\right)_{T_R=1} = +\infty \qquad (10)$$

giving the required slopes at the critical temperature.

COMPUTATIONAL PROCEDURE

Each point for the "tilting capsule" was seen to provide one direct density measurement of relatively high precision. For small θ, and specially with ρ near ρ_c, the θ vs T curve is almost vertical, and T by extrapolation of θ to zero is, therefore, very accurate, as seen in Fig 2. The single point obtained in this instance was ρ_L = 0.4853 g/cc at t = 3225 F. A computational scheme to determine the parameters ρ_c, α_L, α_V, β_L, β_V, γ_L, γ_V, ϵ_L, ϵ_V, T_c that would minimize the sum of the squares of the errors between the observed θ and θ calculated by eq 1 - 3 was set up, subject to the constraint that the liquid density curve was forced to pass through the above density point.

Since θ is a non-linear function of ρ_L and ρ_V and also, since ρ_L and ρ_V are non-linear with respect to the parameters, a direct least squares fit cannot be used. The generalized curve-fitting procedure developed by Marquardt (M 63) was conveniently adapted for this study. This technique basically combines a steepest-descent route together with a Newton-Raphson route for determining improved values of the parameters once initial estimates are provided. This particular set of parameters is somewhat difficult to obtain, mainly because of the large number involved (ten) and, also, because some of them show a somewhat high degree of correlation. In fact, it was relatively easy to obtain a "good" set of parameters but several modifications to the procedure had to be devised before the "best" set was obtained.

The computational procedure is best explained simply as follows. Initial guesses for the parameters (ρ_c, T_c, α_L, α_V, β_L, β_V, γ_L, γ_V, ϵ_L, ϵ_V) are selected. Guesses that give reasonable values for ρ_L and ρ_V are necessary, otherwise the computational scheme tends to stray. ρ_L and ρ_V based on these parameters are calculated at each temperature, corresponding to a data point. The moment equation (eq 1-3) is solved at each data point so that θ_{calc} is available. Increments to the parameters are calculated such that $S = \sum(\theta_{obs} - \theta_{calc})^2$ is reduced. The iterative procedure is repeated until S is minimized.

This method of analysis has the advantage that although the data are in the form of θ vs T, no equation needs to be fitted to θ (T), which would correspond to a smoothing of data, and that the equations for $\rho_L(T)$ and $\rho_V(T)$ are obtained directly.

Saturated Density Results

The data were found to be best represented by the following equations:

$$\rho_L = 0.42051 + 0.33603 (1-T_R) + 1.0061 (1-T_R)^{0.34625} - 0.12416 (1-T_R)^2 \qquad (11)$$

$$\rho_V = 0.42051 + 2.21040 (1-T_R) - 1.3885 (1-T_R)^{0.41809} - 2.26770 (1-T_R)^2 \qquad (12)$$

for ρ_L, ρ_V in g/cc, $T_R = T/T_c$, T_c=3686.03 R.

The tilt angle, θ, fit vs T is shown in Fig 2 and also in Table I. A standard deviation of 0.58 degrees was calculated for θ, which is roughly equal to the accuracy expected in the measurement of θ. The critical density and temperature, obtained directly as parameters, are ρ_c = 0.42051 ± 0.02 g/cc and T_c = 3686.03 ± 1 R.

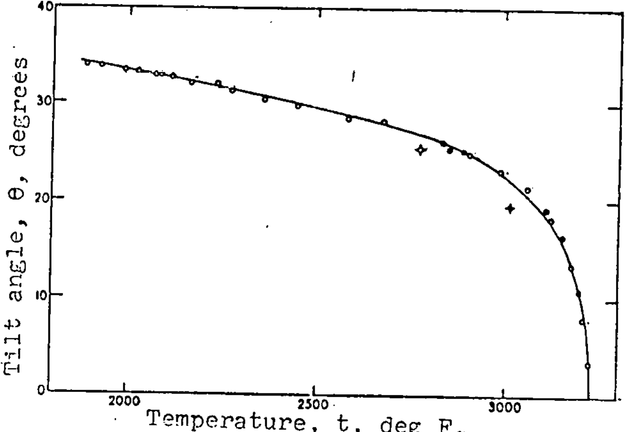

Fig.2 Tilt of cesium capsule from horizontal as a function of temperature. Temperature increasing: O; decreasing: •. Rejected points: +. From Oster (O 67,70).

The density co-existence curves (eq 11,12) are plotted in Fig 3 together with all high temperature data (t > 1800 F) reported.* Dillon's data show large scatter but the calculated ρ_L, ρ_V curves agree well with other reported data. The high temperature vapor and liquid densities predicted by Ewing (E 71) and Miller (M-67a) are compared with those calculated here in Fig 4. It is seen that although there is good agreement between $\rho_V(T)$ calculated in this study and by Ewing or Miller, the specific values of $\rho_L(T)$ predicted by Ewing and by Miller are

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Table II facilitates use of eq 11 and 12.

TABLE I AGREEMENT BETWEEN OBSERVED TILT ANGLE OF CESIUM CAPSULE RUN AND LEAST SQUARES CALCULATED TILT ANGLE BASED ON PHASE DENSITY CORRELATION EQUATIONS

(Excludes two rejected points shown on Fig 2)

Temperature F	Angle, θ degrees Observed	Calculated	Difference	Density, Grams/cc Liquid	Vapor	Average
1884.0	33.90	34.10	-0.20	1.23559	0.01458	0.62509
1923.0	33.80	33.80	0.00	1.22578	0.01956	0.62267
1987.0	33.40	33.33	0.07	1.20930	0.02707	0.61819
2023.0	33.20	33.07	0.13	1.19981	0.03094	0.61488
2070.0	32.90	32.73	0.17	1.18719	0.03563	0.61141
2085.0	32.90	32.63	0.27	1.18310	0.03705	0.61008
2114.0	32.70	32.43	0.27	1.17510	0.03967	0.60739
2165.0	32.10	32.07	0.03	1.16075	0.04393	0.60234
2234.0	32.00	31.60	0.40	1.14072	0.04907	0.59490
2272.0	31.30	31.34	-0.04	1.12935	0.05162	0.59049
2357.0	30.40	30.76	-0.36	1.10299	0.05671	0.57985
2444.0	29.80	30.13	-0.33	1.07450	0.06125	0.56788
2582.0	28.50	29.02	-0.52	1.02549	0.06796	0.54673
2676.0	28.30	28.13	0.17	0.98872	0.07306	0.53089
2832.0	26.10	26.17	-0.07	0.91907	0.08566	0.50237
2851.0	25.40	25.87	-0.47	0.90961	0.08785	0.49873
2886.0	25.20	25.27	-0.07	0.89144	0.09247	0.49196
2902.0	24.90	24.97	-0.07	0.88279	0.09487	0.48883
2988.0	23.20	23.03	0.17	0.83151	0.11212	0.47182
3059.0	21.50	20.77	0.73	0.78037	0.13508	0.45773
3111.0	19.20	18.43	0.77	0.73407	0.16127	0.44767
3122.0	18.30	17.85	0.45	0.72275	0.16847	0.44561
3152.0	16.50	15.87	0.63	0.68763	0.19271	0.44017
3176.0	13.60	13.60	0.00	0.65258	0.21965	0.43612
3195.0	10.90	11.25	-0.35	0.61642	0.24998	0.43320
3205.0	8.00	9.57	-1.57	0.59145	0.27216	0.43181
3219.0	3.50	3.50	0.00	0.53793	0.32185	0.42989
3225*	0.0	0.0	0.0	0.4853		

*By extrapolation.

TABLE II INTERPOLATION TABLE FOR SATURATED LIQUID DENSITY (EQ 11) AND VAPOR DENSITY (EQ 12) OF CESIUM FROM 2400 R TO THE CRITICAL POINT.

(Density in g/cc; Temperature T in degrees R)

T	ρ_L	ρ_V	T	ρ_L	ρ_V
2400.0	1.221368	0.021674	3060.0	1.018570	0.068882
2420.0	1.216229	0.024039	3080.0	1.010884	0.069922
2440.0	1.211044	0.026324	3100.0	1.003058	0.071002
2460.0	1.205811	0.028531	3120.0	0.995085	0.072131
2480.0	1.200530	0.030661	3140.0	0.986956	0.073319
2500.0	1.195198	0.032716	3160.0	0.978661	0.074577
2520.0	1.189816	0.034697	3180.0	0.970191	0.075919
2540.0	1.184381	0.036607	3200.0	0.961534	0.077357
2560.0	1.178892	0.038445	3220.0	0.952679	0.078907
2580.0	1.173349	0.040215	3240.0	0.943612	0.080585
2600.0	1.167749	0.041919	3260.0	0.934316	0.082411
2620.0	1.162092	0.043557	3280.0	0.924776	0.084406
2640.0	1.156375	0.045134	3300.0	0.914970	0.086594
2660.0	1.150597	0.046649	3320.0	0.904877	0.089001
2680.0	1.144756	0.048106	3340.0	0.894471	0.091659
2700.0	1.138849	0.049508	3360.0	0.883721	0.094604
2720.0	1.132877	0.050855	3380.0	0.872594	0.097876
2740.0	1.126836	0.052152	3400.0	0.861047	0.101527
2760.0	1.120724	0.053401	3420.0	0.849034	0.105611
2780.0	1.114539	0.054605	3440.0	0.836493	0.110200
2800.0	1.108277	0.055767	3460.0	0.823355	0.115376
2820.0	1.101938	0.056890	3480.0	0.809528	0.121244
2840.0	1.095518	0.057978	3500.0	0.794902	0.127935
2860.0	1.089015	0.059035	3520.0	0.779328	0.135617
2880.0	1.082424	0.060063	3540.0	0.762611	0.144514
2900.0	1.075743	0.061069	3560.0	0.744480	0.154930
2920.0	1.068969	0.062056	3580.0	0.724543	0.167305
2940.0	1.062098	0.063028	3600.0	0.702195	0.182306
2960.0	1.055123	0.063992	3620.0	0.676421	0.201040
2980.0	1.048044	0.064952	3640.0	0.645265	0.225596
3000.0	1.040854	0.065915	3660.0	0.603943	0.260958
3020.0	1.033549	0.066886	3680.0	0.530175	0.329156
3040.0	1.026124	0.067872	3686.0	0.420513	0.420513

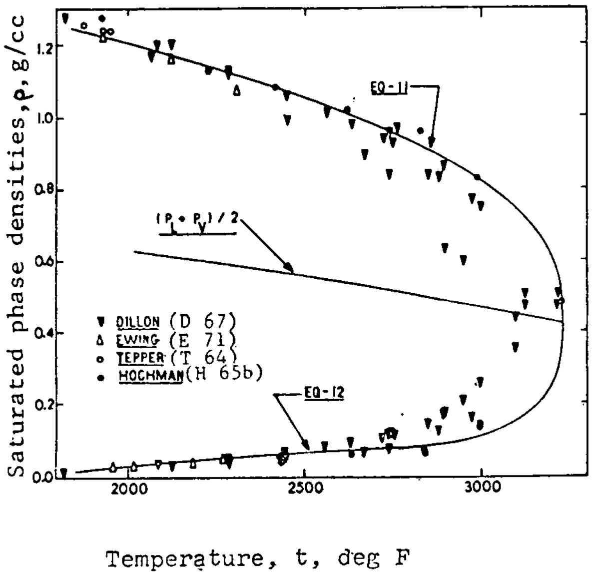

Fig.3 Saturated liquid and vapor phase densities of cesium as a function of temperature.

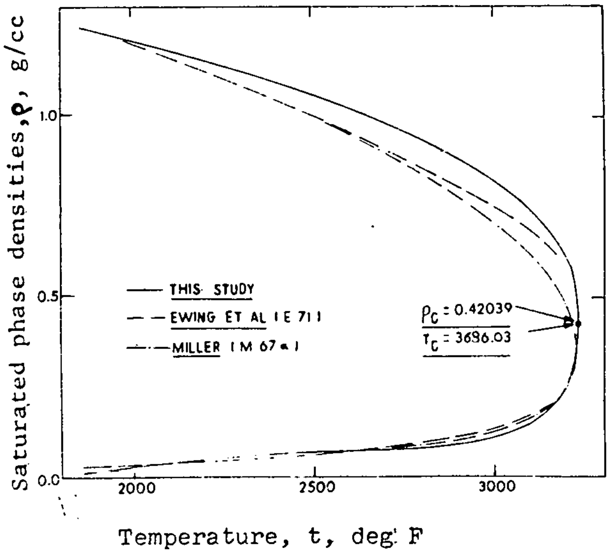

Fig.4 Comparison of Ewing et al (E 71), Miller (M 67a) and present cesium phase densities.

lower. Ewing's $\rho_L(T)$ values at temperatures above 2300 F were calculated by assuming the validity of his rectilinear diameters law, and are, therefore, understandably lower.

The calculated critical density is intermediate between 0.406 g/cc last reported by Oster and Bonilla (O 70) utilizing Ewing's rectilinear diameters line, and Hochman and Bonilla's (H 65b) earlier value of 0.445 g/cc by extrapolation, concurred with in Oster's earlier report (O 67). The cesium was 99.98 +% pure from Dow Chem.Co., analyzing similar to Table III.

VAPOR PRESSURE

The vapor pressure of cesium up to the critical point was apparently first measured by Silver and Bonilla (S 68,70), who determined T_c as 3694.3 R and P_c as 1704 psia, respectively. The only other cesium vapor pressure experiments to claim reaching the critical point were by Hensel et al (H 71, 68) and reported T_c as 3641.7 R and P_c as 1606.4 psia. In view of this discrepancy, added experiments were conducted in this laboratory with improved equipment.

The same "pressure-tube" concept used in Silver's earlier experiments, was used. However, improved furnaces and controls and procedures, solid tungsten pressure tubes, etc., are now in use and excellent results were obtained with potassium using this identical arrangement (J 72,73). Metal analysis is in Table III.

Experimental Results

This set of experiments, shown in Table IV, yielded 33 new vapor pressure points, including 5 at supercritical temperatures. These points are plotted in Fig 5 together with the earlier values, including also other high temperature data. It is seen that these new data are self-consistent and also agree well with Silver's data. Both these and Silver's data are consistently lower than Ewing's except for Ewing's 4 highest temperature points. Unfortunately, because of problems in reading thermocouple outputs at temperatures above 2850 F in this series of runs, it was not possible to reverify Silver's temperature data above 2800 F. However, very good agreement is observed between these and Silver's data up to 2800 F, and the accuracy of Silver's data should improve with increasing temperatures. Thus it seems reasonable to deduce that Silver's data are accurate and that Ewing's data are appreciably high in the range 2000-2900 F. Interestingly, however, Ewing's best fit vapor pressure equation:

$$\log_{10}P = 5.87055 - 7036.2/T - 0.5329 \log T \qquad (13)$$

extrapolates to the same critical point as obtained in this study, approximately.

It is difficult to hypothesize on why Ewing's careful study could yield higher vapor pressures. However, descriptions of their apparatus (E 66,70) suggest that their reported temperatures can be lower than their effective value. They assumed their vertical temperature gradient negligible, since their top and bottom thermocouples on the measurement chamber agreed. But with radial heating, the temperature in the chamber, thus of the vapor-liquid interface, could exceed that at top and bottom, and the liquid would be hydrodynamically stable. This would explain the apparent upward shift of their vapor pressure points on Fig 5. Also, the unexplained "depression phenomenon," in the same direction, observed in some of their runs (which they did not utilize) at the intersection of their saturation and superheat curves, adds weight to the above argument, since the "depressions" are as high as 5 psi. At relatively higher temperatures, however, increased radiation heat transfer tends to flatten out the internal temperature differences, which would account for their highest points agreeing with ours.

TABLE III ANALYSIS OF CESIUM USED IN VAPOR PRESSURE EXPERIMENTS

Al,Mg,Ni	0.0003%	each
Ba,Sn	<0.0008	each
B	<0.0016	
Ca	0.0023	
Cu	0.0008	
Cr,Pb,Sr,Te,Ti	<0.0002	each
Fe	0.0018	
Mn	0.0005	
Si	0.0013	
Li	0.0016	
Na	0.0040	
K	0.0006	
Rb	0.0015	

The data of Hensel and Franck (H68,71) show still a steeper slope than Ewing, but also cross our data near 3400 R, as seen in Fig 5. However, their method for vapor pressure seems to require interpolation of a decreasing temperature on top of their cell to obtain the condensing temperature of the vapor inside. With also a condensing film thermal resistance present under the top, too low a temperature, or alternatively too high a pressure, might well be observed, not a true equilibrium point. Also, cessation of turbulence - their indicator of the critical point - may be imprecise for this purpose; turbulence has been observed in our apparatus below the critical range. Their agreement with our highest points supports above thought. Their operation in cooling mode might agree throughout.

Critical Pressure

Though it was not possible in this study to obtain any temperature readings above 2850 F, it was possible to recheck the critical pressure reported by Silver without benefit of temperature data. The furnace was set at successively higher powers, sufficient to surmount the range in which the break pressure increased with power. Here the observed "break" in the pressure-displacement curve must correspond to the critical pressure. Table IV again shows close agreement with Silver. The averaged value of the critical pressure is 1701.34 psia with a standard deviation of 2.98 psia (0.175%). Combined with 1.7 psia expected instrument error (0.1%) and an extrapolation error of 1 psia, the uncertainty in the critical pressure is calculated as 3.58 psia (0.21%).

Correlation of the Vapor Pressure Data

The starting point for correlating vapor pressure data is generally the Clausius equation

$$\frac{dP}{dT} = \frac{\Delta H_V}{T(v_V - v_L)} \qquad (14)$$

where P_V is the saturation vapor pressure, ΔH_V the latent heat of vaporization, v_V and v_L the specific volume of vapor and liquid, respectively. If eq 14 is rewritten as

$$\frac{d \ln P}{d(1/T)} = -\frac{1}{R}\frac{\Delta H_V}{\Delta Z} \qquad (15)$$

any equation to fit the vapor pressure data can be selected by determining the temperature variation of $(\Delta H_V/\Delta Z)$, where ΔZ is, of course, the change in the compressibility factor Z. A linear dependence of $(\Delta H_V/\Delta Z)$ on temperature leads to the Kirchoff equation:

$$\ln p = A + B/T + C \ln T \qquad (16)$$

The Kirchoff equation, however, does not predict an inflexion in the ln P vs 1/T plot, which must exist from published $(\Delta H_V/\Delta Z)$ values vs T_R for water and several hydrocarbons (T 66,T 50,W 54) (Fig 6). The data collected in this laboratory for rubidium (B 69,B 73) and potassium (J 72,J 73) indicate the existence of an inflexion point. Also, it is found that an extra term of the form DT^m, added to the Kirchoff equation, substantially improves the quality of the fit, roughly halving the standard deviation. Consequently, the composite data were fitted to the same form of equation used by Silver:

$$\ln P = A + B/T + C \ln T + DT^m \qquad (17)$$

where Silver obtained:

$$\ln P = -75.8496 + 7244.83/T + 10.0682 \ln T - 4.49072 \times 10^{-13} T^{3.5} \qquad (18)$$

as his best-fit equation.

Since close agreement is obtained between these and Silver's data (both with the Heise pressure gauge) an equation was fitted to the composite data, eliminating only 3 points of discrepancy $> 5\sigma$.

The exponent 'm' was varied over the range -5 to + 25 to determine its best value. The calculations verified that m = 3.5 (Silver's value) gives a good fit, that is improved only very slightly by increasing 'm'. However, eq 13 does not fit the critical region points well. Therefore, 'm' was selected to fit the high temperature points well without sacrificing the quality of the fit at all temperatures. The best-fit equation thus obtained for the composite data is eq 19, and has $\sigma = 0.81\%$.

$$\ln P = 1.64886421 - 12322.3886/T + 1.12000716 \ln T - 2.90438275 \times 10^{-64} T^{17.5} \qquad (19)$$

The best linear equation, in Fig 5, has $\sigma = 1.09\%$.

Using an average P_c of 1701.34 psia, eq 19 gives $T_c = 3701.75$ R. In fitting the highest temperature points better, the extrapolated T_c (3699.09 R vs 3694.3 R) and point of inflexion (3091 R vs 2967 R) are

TABLE IV

COMPARISON OF EXPERIMENTAL VAPOR PRESSURE POINTS FOR CESIUM WITH CORRELATING EQUATIONS

(Sub-critical Points Only)

		Experimental Data		Pressure by Correlating Equations		$(\Delta H_o^o)_V$
Date	Point No.	Temperature (F)	Pressure (psia)	Eq 18 (psia)	Eq 19 (psia)	Eq 20 (cal/g atom)
8/31/72	A1	2199.34	349.80	341.94	346.03	19404.50
"	A2	2661.97	813.60	827.10	815.82	19357.42
"	A3	2540.92	675.80	673.19	670.22	19349.46
9/2/72	B1	2432.22	549.80	551.04	551.65	19408.57
8/31/72	A4	2750.38	920.80*	950.33	940.57	19369.53
9/2/72	B2	2592.96	729.80	737.13	732.27	19367.21
9/8/72	C1	2776.88	966.80	988.84	978.57	19333.93
"	C2	2836.51	1055.50	1077.82	1066.38	19310.59
"	C3	2711.01	876.80	894.41	885.64	19349.37
"	C4	2059.95	249.80	245.64	248.56	19419.90
"	C5	2099.73	276.80	273.34	276.87	19434.38
"	C6	2202.55	347.80	344.35	348.44	19436.44
"	C7	2289.34	422.80	414.38	417.94	19393.75
"	C8	2493.95	610.80	618.49	617.16	19413.61
"	C9	2376.43	503.80	494.45	496.50	19371.63
"	C10	2473.68	592.80	595.78	595.12	19400.73
"	C11	2510.62	638.80	637.57	635.67	19367.14
"	C12	2255.69	391.80	386.09	383.97	19415.52
"	C13	2297.86	421.80	421.77	425.23	19443.93
"	C14	2336.77	455.80	456.75	459.60	19439.22
"	C15	2416.19	529.80	534.35	535.41	19431.33
"	C16	2543.73	663.80	676.55	673.48	19412.36
"	C17	2579.23	710.80	719.92	715.57	19380.57
"	C18	2610.29	756.80	759.18	753.69	19340.69
"	C19	2627.13	771.80	780.96	774.87	19358.56
"	C20	2649.76	802.80	810.76	803.90	19343.99
"	C21	2694.96	861.80	872.09	863.77	19333.72
"	C22	2754.47	950.80	956.23	946.38	19291.77
1967/68	S1	2536.40	644.90*	667.80	664.99	19459.62
"	S2	2604.00	754.70	751.13	745.87	19320.91
"	S3	2789.20	997.40	1006.97	996.50	19291.17
"	S4	2855.60	1099.20	1106.91	1095.92	19263.09
"	S5	2939.00	1257.60 *	1236.75	1226.54	19170.57
"	S6	2995.30	1355.30 *	1326.22	1317.32	19145.94
"	S7	3052.20	1402.60	1417.32	1410.06	19243.40
"	S8	3128.50	1532.90	1539.17	1533.48	19227.71
"	S9	3161.10	1607.30	1621.98	1615.72	19254.16
"	S10	3216.30	1668.50	1676.45	1668.32	19250.11
"	S11	3081.30	1461.70	1463.92	1457.44	19215.42
"	S12	3020.60	1366.90	1366.69	1358.51	19211.05
"	S13	2949.30	1250.90	1253.04	1243.02	19200.92
"	S14	2880.20	1127.20	1144.78	1133.85	19282.41
"	S15	2829.80	1064.30	1067.66	1056.75	19259.03
"	S16	2758.90	957.50	962.64	952.70	19289.17
"	S17	2726.80	912.90	916.65	907.45	19297.24
"	S18	2667.40	840.90	834.42	826.97	19285.17
"	S19	2616.60	777.40 *	769.68	764.10	19300.68
"	S20	2397.00	516.40	514.83	516.39	19406.66
"	S21	2009.00	220.30	220.65	222.79	19455.42
"	S22	2385.30	509.90	503.17	505.01	19383.18
"	S23	2619.00	764.60	770.40	764.60	19349.74
"	S24	2791.90	991.80	1010.97	1000.45	19318.86
"	S25	2955.40	1253.60	1262.70	1252.82	19241.68
"	S26	3147.80	1573.50	1569.71	1564.05	19209.58
"	S27	3221.80	1672.60	1684.88	1676.30	19261.54

*Not included in the curve-fit due to large deviations from smooth curve.

Note: 1972 points by Das Gupta (D 72), 1967/68 points by Silver (S 67,70).

increased.

The vapor-pressure values calculated by eq 13 and eq 19 are compared with the data in Table IV. Table V gives the vapor pressure based on eq 19, every 10 F for interpolation purposes. Table VI compares the reported correlating equations with the Hensel et al points (H 68,71), who did not provide an equation.

Internal Thermodynamic Consistency

An independent check on the internal consistency of the vapor pressure data was carried out using the standard Third Law test:

$$(\Delta H_0^o)_V = - RT \ln P_{1,S} - T\left[\left\{\left(\frac{h_T^o - h_0^o}{T}\right)_L - \left(\frac{h_T^o - h_0^o}{T}\right)_V\right\} - \left\{(S_T^o)_L - (S_T^o)_V\right\}\right] \quad (20)$$

where $P_{1,S} = \frac{-1 + \sqrt{4\,K\,P + 1}}{2K}$ and P is in atm. Since the specific heat of liquid cesium is not known accurately over the entire range, a constant value of C_{PL} = 0.05621 cal/g was used. The standard enthalpy functions and entropies were calculated based on formulae reported by Ewing et al (E 65).

$(\Delta H_0^o)_V$, the standard heat of vaporization of monomeric species, calculated at each vapor pressure point, is shown in Table IV. The average $(\Delta H_0^o)_V$ is 19.337 K cal/g-atom with a standard deviation of 0.37%.

ACKNOWLEDGEMENT

This work was supported by the Division of Research of the U.S. Atomic Energy Commission under contract AT(11-1)-3027 with Columbia University. This article is designated report COO-3027-9.

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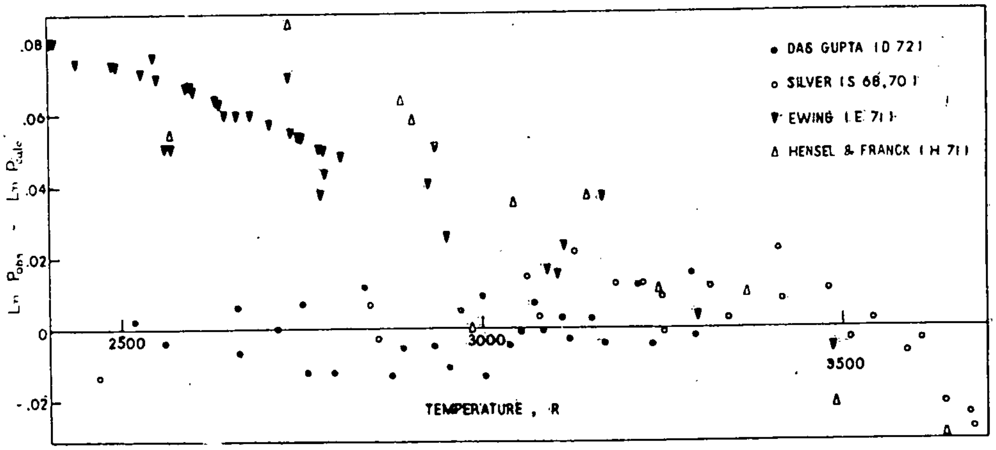

Fig.5 Deviation of cesium vapor pressure data from linear Least Squares correlation of Silver and Das Gupta data: $\ln P_{calc} = 11.60857 - 15308.32/T$

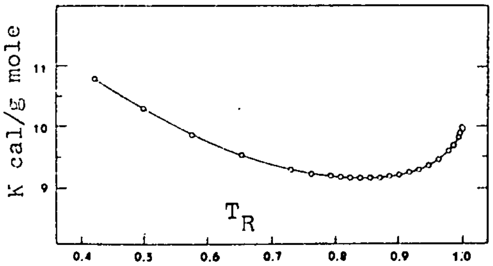

Fig.6 $\Delta H_V/\Delta Z$ for water as a function of reduced temperature (W 54).

TABLE IV

OBSERVED CRITICAL PRESSURES BY HEISE GAUGE

		Averages
Silver	1699.7	1700.7
"	1701.7	
This study	1705.8	1701.6
"	1698.8	
"	1701.8	
"	1696.8	
"	1704.8	
Average	1701.34 psia	
Standard Deviation	2.98 psia	

TABLE V

INTERPOLATION TABLE FOR VAPOR PRESSURE OF CESIUM FROM 2000 F TO THE CRITICAL POINT

$$\ln P = 1.64886421 - 12322.3886 + 1.12000716 \ln T - 2.90438275 \times 10^{-64}\ T^{17.5}$$

(P in lbs/sq in.abs; T in degrees R)

T	P	T	P	T	P	T	P
2400.00	187.12	2730.00	401.95	3060.00	741.30	3390.00	1212.66
2410.00	192.04	2740.00	410.30	3070.00	753.71	3400.00	1228.61
2420.00	197.05	2750.00	418.75	3080.00	766.24	3410.00	1244.63
2430.00	202.16	2760.00	427.33	3090.00	778.90	3420.00	1260.70
2440.00	207.35	2770.00	436.02	3100.00	791.69	3430.00	1276.82
2450.00	212.64	2780.00	444.83	3110.00	804.60	3440.00	1292.99
2460.00	218.03	2790.00	453.76	3120.00	817.64	3450.00	1309.20
2470.00	223.51	2800.00	462.81	3130.00	830.80	3460.00	1325.45
2480.00	229.08	2810.00	471.98	3140.00	844.08	3470.00	1341.72
2490.00	234.75	2820.00	481.26	3150.00	857.49	3480.00	1358.02
2500.00	240.52	2830.00	490.67	3160.00	871.01	3490.00	1374.33
2510.00	246.39	2840.00	500.20	3170.00	884.66	3500.00	1390.65
2520.00	252.36	2850.00	509.85	3180.00	898.44	3510.00	1406.96
2530.00	258.42	2860.00	519.63	3190.00	912.33	3520.00	1423.27
2540.00	264.59	2870.00	529.52	3200.00	926.33	3530.00	1439.56
2550.00	270.86	2880.00	539.54	3210.00	940.46	3540.00	1455.82
2560.00	277.23	2890.00	549.68	3220.00	954.70	3550.00	1472.04
2570.00	283.71	2900.00	559.95	3230.00	969.06	3560.00	1488.22
2580.00	290.29	2910.00	570.34	3240.00	983.53	3570.00	1504.33
2590.00	296.97	2920.00	580.86	3250.00	998.11	3580.00	1520.38
2600.00	303.76	2930.00	591.50	3260.00	1012.80	3590.00	1536.35
2610.00	310.65	2940.00	602.26	3270.00	1027.59	3600.00	1552.22
2620.00	317.66	2950.00	613.15	3280.00	1042.50	3610.00	1567.98
2630.00	324.77	2960.00	624.17	3290.00	1057.51	3620.00	1583.63
2640.00	331.98	2970.00	635.32	3300.00	1072.61	3630.00	1599.14
2650.00	339.31	2980.00	646.58	3310.00	1087.82	3640.00	1614.50
2660.00	346.75	2990.00	657.98	3320.00	1103.12	3650.00	1629.69
2670.00	354.30	3000.00	669.50	3330.00	1118.52	3660.00	1644.71
2680.00	361.96	3010.00	681.15	3340.00	1134.00	3670.00	1659.53
2690.00	369.73	3020.00	692.93	3350.00	1149.58	3680.00	1674.13
2700.00	377.62	3030.00	704.83	3360.00	1165.23	3690.00	1688.50
2710.00	385.61	3040.00	716.86	3370.00	1180.97	3699.09	1701.34
2720.00	393.73	3050.00	729.02	3380.00	1196.78		

From: S. Das Gupta, V. Bhise, D.W. Stuteville, J.-W. Chung, C.F. Bonilla, Sixth Symposium on Thermophysical Properties, ASME, Atlanta (1973)

TABLE VI

COMPARISON OF THE CESIUM VAPOR PRESSURE DATA OF HENSEL AND FRANCK (H 68,71) WITH THE PRESENT CORRELATION (EQ 19) AND THOSE OF SILVER (EQ 18) AND EWING ET AL (EQ 13)

		Pressure, P				
Temperature, T		Hensel & Franck		Ewing et al	Silver	This Study
				(Eq 13)	(Eq 18)	(Eq 19)
(°C)	(°R)	(bars)	(psia)	(psia)	(psia)	(psia)
1020	2327.7	10.8	156.6	166.2	(155.2)	(153.9)
1153	2567.1	20.6	298.8	302.0	278.2	281.1
1245	2732.7	30.5	552.5	428.1	400.5	403.4
1331	2887.5	40.3	584.5	571.3	546.4	546.8
1340	2903.7	41.3	599.0	587.7	563.5	563.5
1386	2986.5	45.1	654.1	675.8	656.5	654.1
1417	3042.3	51.3	744.0	739.2	724.2	720.1
1476	3148.5	60.9	883.3	868.6	863.6	856.5
1531	3247.5	68.8	997.9	999.5	1004.9	996.1
1600	3371.7	81.7	1185.0	1177.4	1194.3	1185.4
1665	3488.7	92.3	1338.7	1358.3	1380.2	1373.0
1750	3641.7	110.0	1595.4	1613.7	1623.5	1614.8