ACKNOWLEDGMENT

NOMENCLATURE AND UNITS

B = second virial coefficient, cu. ft. per mole
C = third virial coefficient, (cu. ft.)^2 per (mole)^2
D = fourth virial coefficient, (cu. ft.)^3 per (mole)^3
c_p = specific heat at constant pressure, B.t.u. per lb.-° F.
f = free energy, B.t.u. per lb.
h = enthalpy per unit mass, B.t.u. per lb.
Δh_v = enthalpy change upon vaporization of a unit mass of equilibrium vapor, B.t.u. per lb.
ΔH_v = enthalpy change upon vaporization of a mole of equilibrium vapor, B.t.u. per lb.-mole
J = any unit conversion
M_1 = molecular weight of monomeric species
p = absolute pressure, lb. per sq. inch
R = gas constant
s = entropy per unit mass, B.t.u. per lb.-° F.
Δs_v = entropy change upon vaporization of a unit mass of equilibrium vapor, B.t.u. per lb.-° F.
T = absolute temperature, ° R.
t = temperature, ° F.
$\tilde{V}$ = molal volume (per formula weight of monomer), cu. ft. per lb.-mole
v = specific volume, cu. ft. per lb.
z = compressibility factor, $p\tilde{V}/RT$

Subscripts

0 = quantity at 0° R.
p = constant pressure change
s = quantity at saturation

Superscripts

g = quantity in gas state
l = quantity in liquid state
$°$ = standard state, 1 atm. for gas

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High-Temperature Properties of Cesium

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A virial equation of state for cesium with coefficients through the fifth virial is derived from compressibility data covering a temperature range from 1305° to 2550° F. and a pressure range from 16.5 to 487.9 p.s.i.a. Exact thermodynamic relationships involving the virial and vapor-pressure equations are used to generate saturation and superheat properties of the vapor. Values of the enthalpy, entropy, specific heat, and specific volume are tabulated for some 280 selected states in the temperature range from 1250° to 2550° F. and in the pressure range from 2.9 to 499.7 p.s.i.a. The thermal properties from 1050° to 2550° F. are also presented as a Mollier diagram.

DESIGN STUDIES of high-temperature power-converters employing alkali metal vapors as working fluids require an improved knowledge of their thermodynamic properties. In response to this need, experimental PVT, vapor-pressure, and liquid density data for three metals—sodium, potassium, and cesium—have been measured by Stone et al. (9, 10, 11). From the data for two of the metals, sodium and potassium, the authors have generated and published consistent sets of thermodynamic properties (5, 6). The present article extends this work to the third metal, cesium.

TREATMENT OF PVT DATA

Derivation of Virial Coefficients. Coefficients for the cesium equation of state in its volume expansion form (Equation 1) were derived from the experimental PVT data of Stone et al. (9), which cover a temperature range in the superheat region from 1305° to 2550° F. They were obtained graphically as described for potassium (5) by plotting experimental functions along constant temperature lines. However, two modifications of the method were required for cesium. First, the adjustment procedure (5), which was

helpful in defining virial coefficients at lower temperatures for sodium and potassium, was not required since data for cesium were more numerous and more precise than those reported for the other metals. In the second place, an additional virial coefficient—the fifth—was required for cesium in order to obtain a precise fit to all the data along any given isotherm. Only a rough value of the higher virial was required, and this was also obtained by a graphical procedure. The quantity $[(z - 1)$ $\tilde{V}^3 - B\tilde{V}^2 - C\tilde{V}]$ was plotted $vs.$ $1/\tilde{V}$ at several higher temperatures using preliminary values for the lower virial coefficients; the average slope (600,000) at higher pressures was taken as the value of E.

The Virial Equation of State for Cesium. The equation of state, obtained as described above, is

$$\frac{p\tilde{V}}{RT} = 1 + \frac{B}{\tilde{V}} + \frac{C}{\tilde{V}^2} + \frac{D}{\tilde{V}^3} + \frac{E}{\tilde{V}^4} \qquad (1)$$

where,

$$\log|B| = -3.6200 + 4000.0/T + \log T$$
$$B < 0$$
$$\log C = 3.3551 - 5331.5/T + 10.825 \times 10^6/T^2$$
$$C > 0$$
$$\log|D| = 4.1856 + 880/T$$
$$D < 0$$
$$E = 600,000$$

The degree to which the virial equation fits the measured data is shown graphically in Figure 1, in which compressibilities generated with Equation 1 are compared to experimental values at 100° intervals from 1350° to 2550° F. The
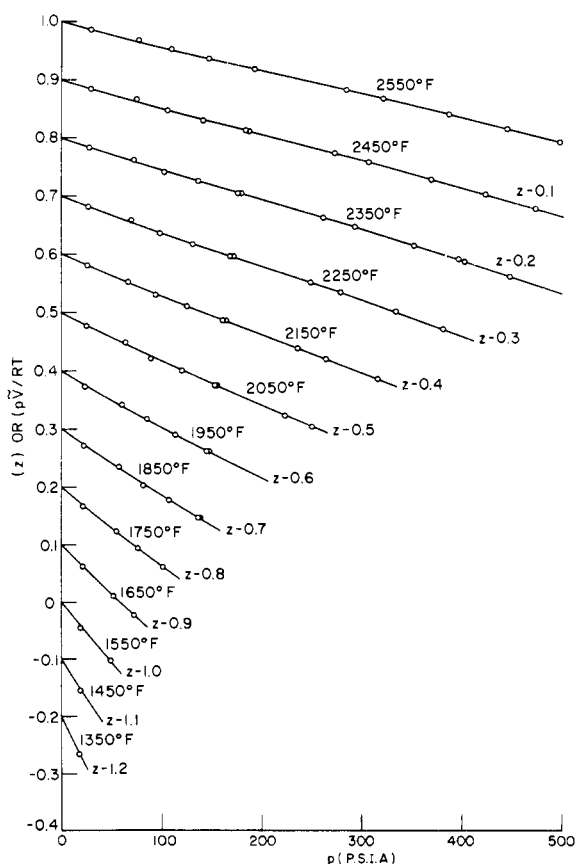
Figure 1. Compressibility of cesium vapor at several temperatures

degree of fit also can be shown mathematically. For example, all the observed compressibility data for cesium reported by Stone et al. (9) may be calculated from the virial equation with a standard per cent deviation of only ±0.22.

The equation of state was derived from experimental data over a temperature range from 1550° to 2500° F. Data were also obtained in a lower range from 1300° to 1550° F., but the number of experimental points along any given isotherm was insufficient to obtain reliable virial coefficients by the graphical method. Consequently, before the equation of state was acceptable for calculations below 1550° F., it was necessary to determine its fit to the observed low-temperature data. Compressibility factors were calculated and compared to the observed values in this region (Figure 1). The agreement was equivalent to that obtained at higher temperatures.

CALCULATION OF THERMODYNAMIC PROPERTIES AND FUNDAMENTAL DATA

For the design of high-temperature cycles, the important properties of the liquid and vapor are volume, enthalpy, entropy, and specific heat. These properties for cesium were computed from the virial equation of state, from exact thermodynamic relationships, or from the fundamental property equations included in this section.

Saturation Pressure of Liquid Cesium. Pressures at all temperatures were obtained from the vapor-pressure equation of Stone et al. (10). This equation,

$$\log p = 7.04023 - 7040.7/T - 0.53290 \log T \qquad (2)$$

is based on experimentally determined data over the temperature range from the normal boiling point to 2350° F., and is in good agreement with the lower temperature work of Tepper and coworkers (12), Achener (1), and Bonilla, Sawhney, and Makansi (3).

Specific Volume of Liquid Cesium. Values were obtained from the correlating equation of Stone et al. (11). This equation,

$$\frac{1}{v^l} = 124.181 - 1.5970 \times 10^{-3}T - 1.6855 \times 10^{-6}T^2 \qquad (3)$$

was derived from all available data and covers a temperature range from the melting point to 2304° F. The error limit given for the full range was ±0.6%.

Specific Volume of Saturated and Superheated Cesium Vapor. The value of this property at each state was obtained from the virial equation of state.

Enthalpy, Entropy, and Specific Heat of Saturated and Superheated Cesium Vapor. These properties were computed along constant temperature lines from exact thermodynamic relationships with the value of the property for the monomeric gas as a base. The working relationships are the same as those used for potasium (5) except that terms for the fifth virial must be added.

Enthalpy, Entropy, and Specific Heat of Monomeric Cesium Vapor. The monomeric gas properties, together with the

Table I. Summary of Heat Capacity Measurements of Liquid Cesium

Investigator and Reference	Temperature Range, ° F.	Heat Capacity Equation, B.t.u./Lb.-° F.
Achener (1)	152–1656	$c_p^l = 0.08543 - 9.605 \times 10^{-5}t$ $+ 5.985 \times 10^{-8}t^2$
Tepper (12)	620–1770	$c_p^l = 0.0545$
Lemmon (8)	570–2100	$c_p^l = 0.0600$

value selected for the enthalpy of sublimation at absolute zero, largely determine the magnitudes of the superheat properties. The equations for the three properties (relative to the solid crystal at 0° R.) are

$$(h^t)^\circ = 252.18 + 0.037361\ T + 2480\ e^{-31,290/T} \qquad (4)$$

$$(s^t)^\circ = 0.080604 + 0.037361\ \ln T + 0.371\ e^{-28,598/T} \qquad (5)$$

$$(c_p^t)^\circ = 0.037361 + 1.3099\ e^{-25,663/T} \qquad (6)$$

These were derived directly from the work of Evans and coworkers (4) and are based on their standard properties over the temperature range from 0° to 2800° F. and on the enthalpy of sublimation at 0° R. (18.62 mean kcal. per gram atom) as derived in the next section.

Enthalpy of Sublimation of Cesium at 0° R. This quantity is needed to relate the enthalpy of the ideal gas to the base state—solid at 0° R. Since the virial coefficients of cesium are known, a reliable value of the sublimation constant can be obtained from saturation pressure data with the third-law equation,

$$(\Delta H_0^s)_v = -\ RT\left[\frac{2B}{\bar{V}_s} + \frac{3C}{2\bar{V}_s^2} + \frac{4D}{3\bar{V}_s^3} + \frac{5E}{4\bar{V}_s^4} + \ln p_s - \ln \frac{p_s\bar{V}_s}{RT}\right] - $$

$$M_1 T_s\left[\frac{f^\circ - h_0^s}{T}\right]_1^s \qquad (7)$$

Before this can be done, all the thermal functions must be known. The free-energy functions for monomeric cesium gas can be obtained from Evans et al. (4), and corresponding functions for the liquid may be derived from heat-capacity results. Three measurements of liquid heat capacity were found in the literature and pertinent data related to each are summarized in Table I. There is significant disagreement both in the magnitude and the temperature dependency of the specific heat.

Since there was no apparent reason to choose one set of specific-heat data over another, the selected value of both c_p^l and $(\Delta H_0^s)_v$ were based on a third-law analysis of the vapor-pressure measurements of Stone and coworkers (10). Normally, a third-law analysis is used to check the internal consistency of vapor-pressure measurements. In this case, however, the analysis was used to obtain the most consistent values for the specific heat of the liquid and the sublimation constant.

In two preliminary analyses, the value of $(\Delta H_0^s)_v$ was computed from the vapor-pressure data over the temperature range from 1215° to 2346° F. using, in one case a constant liquid specific heat of 0.0545 and, in the other, 0.0600 B.t.u. per lb.-° F. These are the heat capacities reported by Tepper et al. (12) and Lemmon et al. (8), respectively. Thermal data for the solid at 77° F. were taken from Hultgren et al. (7) and at higher temperatures from the work of Lemmon

et al. (8). When the sublimation quantities, so calculated, were plotted against temperature, those based on a liquid specific heat of 0.0600 B.t.u. per lb.-° F. exhibited a constant negative slope while those computed with the other value, a positive slope. It followed that a value of specific heat intermediate between the two, would lead to a generally constant value of $(\Delta H_0^s)_v$ for all the saturation pressures. By a trial and error procedure this value for the liquid specific heat was found to be 0.05683 B.t.u. per lb.-° F. The value of $(\Delta H_0^s)_v$ obtained by this procedure is 18.62 mean kcal. per gram atom. Although the agreement is perhaps fortuitous, this is practically the same as the value of 18.66 published by Hultgren and coworkers (7), which was obtained by a third-law treatment of several vapor-pressure measurements at lower temperatures.

Enthalpy and Entropy of Vaporization of Cesium. Latent heats of vaporization were calculated with

$$\Delta h_v = Jp_s(1103.1/T - 0.036262)\ (v_s^g - v_s^l) \qquad (8)$$

which was derived by a differentiation of Equation 2 and subsequent substitution into the Clapeyron equation. A value of v_s^l at each temperature was obtained from Equation 3 and a value of v_s^g from the virial equation of state (Equation 1).

The heats of vaporization so obtained from the Clapeyron equation are presented graphically in Figure 2 and are compared with values reported by Achener (1). The four results by Achener were measured directly by noting the heat required to vaporize a given mass of the liquid. The
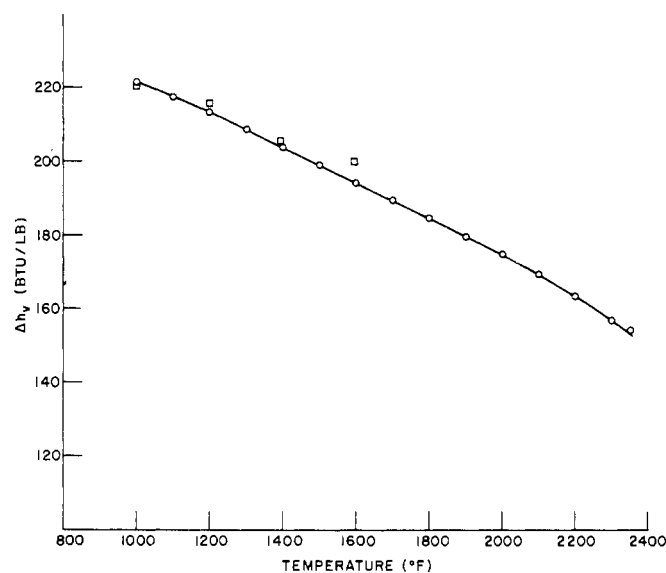
Figure 2. Enthalpy of vaporization of cesium
□ Achener
○ NRL

Table II. Saturation Properties of Cesium[a]

Basis: h = 0 and s = 0 for solid cesium at 0° R.

t	p_s	v^l	v_s^g	h^l	Δh_v	h_s^g	s^l	Δs_v	s_s^g
1300.00	20.40	0.01101	6.3778	97.72	208.70	306.41	0.2310	0.1186	0.3496
1400.00	32.51	0.01128	4.1522	103.81	203.95	307.76	0.2344	0.1097	0.3441
1500.00	49.33	0.01157	2.8289	109.91	199.10	309.01	0.2376	0.1016	0.3392
1600.00	71.78	0.01189	2.0041	115.98	194.24	310.22	0.2406	0.0943	0.3349
1700.00	100.76	0.01222	1.4687	122.01	189.44	311.45	0.2434	0.0877	0.3311
1800.00	137.12	0.01258	1.1083	128.02	184.71	312.73	0.2461	0.0817	0.3278
1900.00	181.60	0.01297	0.8576	134.11	179.92	314.04	0.2487	0.0762	0.3249
2000.00	234.86	0.01339	0.6774	140.43	174.88	315.31	0.2512	0.0711	0.3223
2100.00	297.45	0.01384	0.5440	147.10	169.32	316.43	0.2538	0.0661	0.3200
2200.00	369.80	0.01433	0.4427	154.12	163.11	317.23	0.2564	0.0613	0.3178
2300.00	452.21	0.01487	0.3655	160.91	156.77	317.68	0.2589	0.0568	0.3157

[a] Values are given to more significant figures then the data warrant in order to retain precision in differences.

Figure 3. Mollier diagram for cesium

Table III. Thermodynamic Properties of Cesium Vapor in the Superheat Region[a]

Basis: $h = 0$ and $s = 0$ for solid cesium at 0° R.

p	v^g	z	h^g	s^g	c_p^g

1250° F.

p	v^g	z	h^g	s^g	c_p^g
15.82	8.0598	0.92387	305.69	0.35270	0.0671
14.70	8.7283	0.92917	306.40	0.35414	0.0653
11.76	11.0740	0.94310	308.28	0.35836	0.0604
8.82	14.9858	0.95718	310.19	0.36357	0.0551
5.88	22.8122	0.97138	312.13	0.37055	0.0494
2.94	46.2952	0.98566	314.09	0.38183	0.0435

1350° F.

p	v^g	z	h^g	s^g	c_p^g
25.93	5.1146	0.90742	307.10	0.34675	0.0703
14.70	9.4160	0.94698	312.51	0.35761	0.0572
11.76	11.9009	0.95751	313.95	0.36159	0.0534
8.82	16.0432	0.96809	315.40	0.36653	0.0495
5.88	24.3286	0.97870	316.86	0.37324	0.0455
2.94	49.1860	0.98934	318.33	0.38425	0.0415

1450° F

p	v^g	z	h^g	s^g	c_p^g
40.27	3.4093	0.89040	308.39	0.34152	0.0730
29.39	4.8227	0.91925	312.38	0.34787	0.0645
14.70	10.0656	0.95931	317.92	0.36053	0.0514
11.76	12.6883	0.96741	319.04	0.36432	0.0486
8.82	17.0599	0.97554	320.16	0.36909	0.0458
5.88	25.8034	0.98368	321.28	0.37561	0.0430
2.94	52.0347	0.99184	322.40	0.38644	0.0402

1550° F.

p	v^g	z	h^g	s^g	c_p^g
59.79	2.3703	0.87335	309.62	0.33694	0.0749
58.78	2.4165	0.87536	309.90	0.33730	0.0744
44.09	3.3324	0.90537	314.11	0.34323	0.0664
29.39	5.1697	0.93636	318.45	0.35097	0.0572
14.70	10.6886	0.96799	322.84	0.36304	0.0474
11.76	13.4488	0.97437	323.73	0.36672	0.0454
8.82	18.0493	0.98076	324.61	0.37136	0.0434
5.88	27.2508	0.98716	325.50	0.37777	0.0414
2.94	54.8557	0.99358	326.38	0.38847	0.0394

1650° F.

p	v^g	z	h^g	s^g	c_p^g
85.40	1.7089	0.85672	310.83	0.33292	0.0761
73.48	2.0295	0.87542	313.50	0.33613	0.0719
58.78	2.6059	0.89924	316.90	0.34070	0.0658
44.09	3.5692	0.92376	320.37	0.34627	0.0591
29.39	5.4990	0.94881	323.89	0.35362	0.0520
14.70	11.2931	0.97426	327.44	0.36527	0.0447
11.76	14.1907	0.97939	328.15	0.36887	0.0433
8.82	19.0202	0.98453	328.87	0.37343	0.0418
5.88	28.6795	0.98967	329.58	0.37975	0.0403
2.94	57.6580	0.99483	330.29	0.39037	0.0388

1750° F.

p	v^g	z	h^g	s^g	c_p^g
117.97	1.2715	0.84071	312.08	0.32940	0.0766
117.57	1.2766	0.84120	312.15	0.32948	0.0765
102.87	1.4905	0.85939	314.79	0.33236	0.0730
88.18	1.7770	0.87817	317.51	0.33560	0.0688
73.48	2.1793	0.89749	320.29	0.33928	0.0641
58.78	2.7842	0.91728	323.13	0.34359	0.0591
44.09	3.7940	0.93748	326.00	0.34888	0.0538
29.39	5.8157	0.95804	328.90	0.35594	0.0484
14.70	11.8846	0.97889	331.82	0.36730	0.0429
11.76	14.9196	0.98309	332.40	0.37084	0.0418
8.82	19.9780	0.98731	332.99	0.37534	0.0407
5.88	30.0952	0.99153	333.57	0.38160	0.0396
2.94	60.4472	0.99576	334.15	0.39216	0.0385

1850° F

p	v^g	z	h^g	s^g	c_p^g
158.30	0.9721	0.82515	313.38	0.32631	0.0765
146.96	1.0615	0.83643	315.02	0.32795	0.0748
132.26	1.2005	0.85136	317.19	0.33022	0.0721
117.57	1.3747	0.86664	319.43	0.33270	0.0691
102.87	1.5994	0.88225	321.71	0.33543	0.0620
88.18	1.8997	0.89820	324.03	0.33849	0.0582
73.48	2.3210	0.91446	326.39	0.34198	0.0541
58.78	2.9538	0.93103	328.78	0.34609	0.0541
44.09	4.0097	0.94789	331.18	0.35117	0.0500
29.39	6.1232	0.96501	333.61	0.35802	0.0458
14.70	12.4669	0.98239	336.04	0.36917	0.0416
11.76	15.6392	0.98590	336.53	0.37266	0.0408

1850° F. cont.

p	v^g	z	h^g	s^g	c_p^g
8.82	20.9266	0.98941	337.01	0.37712	0.0399
5.88	31.5016	0.99293	337.50	0.38334	0.0391
2.94	63.2272	0.99646	337.99	0.39385	0.0382

1950° F.

p	v^g	z	h^g	s^g	c_p^g
207.09	0.7604	0.80936	314.68	0.32358	0.0760
205.74	0.7665	0.81049	314.85	0.32373	0.0759
191.05	0.8380	0.82286	316.61	0.32537	0.0744
176.35	0.9217	0.83535	318.42	0.32711	0.0725
161.66	1.0206	0.84797	320.27	0.32897	0.0704
146.96	1.1396	0.86076	322.15	0.33097	0.0681
132.26	1.2853	0.87373	324.06	0.33313	0.0655
117.57	1.4678	0.88689	326.01	0.33549	0.0627
102.87	1.7027	0.90025	327.97	0.33809	0.0598
88.18	2.0165	0.91383	329.96	0.34100	0.0568
73.48	2.4563	0.92764	331.97	0.34434	0.0537
58.78	3.1169	0.94166	334.00	0.34830	0.0505
44.09	4.2187	0.95592	336.04	0.35323	0.0472
29.39	6.4239	0.97039	338.09	0.35992	0.0440
14.70	13.0424	0.98509	340.15	0.37091	0.0407
11.76	16.3521	0.98806	340.56	0.37437	0.0400
8.82	21.8684	0.99103	340.97	0.37880	0.0394
5.88	32.9013	0.99401	341.39	0.38498	0.0387
2.94	66.0005	0.99700	341.80	0.39547	0.0380

2050° F.

p	v^g	z	h^g	s^g	c_p^g
264.96	0.6059	0.79227	315.90	0.32113	0.0756
264.53	0.6072	0.79260	315.94	0.32117	0.0756
249.83	0.6518	0.80362	317.47	0.32245	0.0745
235.14	0.7020	0.81458	319.01	0.32380	0.0733
220.44	0.7589	0.82551	320.57	0.32522	0.0718
205.74	0.8238	0.83642	322.15	0.32670	0.0702
191.05	0.8988	0.84734	323.75	0.32827	0.0684
176.35	0.9863	0.85831	325.37	0.32994	0.0665
161.66	1.0898	0.86934	327.01	0.33171	0.0645
146.96	1.2141	0.88045	328.66	0.33362	0.0623
132.26	1.3662	0.89167	330.33	0.33568	0.0601
117.57	1.5565	0.90302	332.02	0.33703	0.0577
102.87	1.8015	0.91452	333.72	0.34042	0.0553
88.18	2.1285	0.92617	335.44	0.34323	0.0529
73.48	2.5869	0.93800	337.16	0.34646	0.0503
58.78	3.2750	0.95001	338.91	0.35030	0.0478
44.09	4.4227	0.96221	340.66	0.35511	0.0452
29.39	6.7196	0.97461	342.42	0.36168	0.0426
14.70	13.6128	0.98721	344.18	0.37255	0.0400
11.76	17.0599	0.98975	344.54	0.37599	0.0395
8.82	22.8051	0.99230	344.89	0.38039	0.0390
5.88	34.2958	0.99486	345.24	0.38655	0.0384
2.94	68.7687	0.99743	345.60	0.39701	0.0379

2150° F.

p	v^g	z	h^g	s^g	c_p^g
332.38	0.4900	0.77288	316.87	0.31886	0.0758
323.31	0.5079	0.77927	317.72	0.31950	0.0753
308.62	0.5391	0.78952	319.10	0.32058	0.0743
293.92	0.5733	0.79961	320.49	0.32169	0.0732
279.22	0.6110	0.80957	321.88	0.32284	0.0721
264.53	0.6527	0.81941	323.27	0.32403	0.0708
249.83	0.6993	0.82915	324.67	0.32527	0.0694
235.14	0.7517	0.83881	326.07	0.32656	0.0679
220.44	0.8110	0.84841	327.48	0.32792	0.0664
205.74	0.8787	0.85797	328.90	0.32934	0.0648
191.05	0.9569	0.86753	330.32	0.33084	0.0631
176.35	1.0480	0.87710	331.76	0.33243	0.0614
161.66	1.1558	0.88671	333.20	0.33413	0.0596
146.96	1.2853	0.89637	334.65	0.33596	0.0577
132.26	1.4436	0.90612	336.12	0.33794	0.0558
117.57	1.6417	0.91597	337.59	0.34011	0.0539
102.87	1.8967	0.92593	339.07	0.34251	0.0519
88.18	2.2369	0.93603	340.57	0.34523	0.0499
73.48	2.7136	0.94627	342.07	0.34837	0.0478
58.78	3.4293	0.95666	343.58	0.35212	0.0458
44.09	4.6229	0.96723	345.10	0.35684	0.0437
29.39	7.0114	0.97797	346.62	0.36332	0.0416
14.70	14.1794	0.98889	348.16	0.37410	0.0395
11.76	17.7638	0.99110	348.46	0.37752	0.0391
8.82	23.7380	0.99331	348.77	0.38191	0.0387
5.88	35.6866	0.99553	349.08	0.38805	0.0383
2.94	71.5330	0.99776	349.39	0.39850	0.0378

Table III. Thermodynamic Properties of Cesium Vapor in the Superheat Region (Continued)

(Basis: $h = 0$ and $s = 0$ for solid cesium at $0°$ R.)

2250° F.

p	v^g	z	h^g	s^g	c_p^g
409.73	0.4014	0.75165	317.49	0.31670	0.0766
396.79	0.4191	0.76009	318.62	0.31749	0.0760
382.10	0.4407	0.76967	319.91	0.31839	0.0751
367.40	0.4640	0.77917	321.20	0.31932	0.0742
352.70	0.4892	0.78856	322.49	0.32028	0.0731
338.01	0.5164	0.79781	323.76	0.32125	0.0720
323.31	0.5461	0.80692	325.04	0.32225	0.0709
308.62	0.5784	0.81589	326.31	0.32329	0.0697
293.92	0.6139	0.82472	327.57	0.32435	0.0684
279.22	0.6531	0.83343	328.83	0.32545	0.0671
264.53	0.6965	0.84203	330.09	0.32660	0.0658
249.83	0.7449	0.85055	331.35	0.32778	0.0644
235.14	0.7993	0.85900	332.61	0.32902	0.0630
220.14	0.8609	0.86739	333.87	0.33032	0.0616
205.74	0.9313	0.87576	335.14	0.33169	0.0602
191.05	1.0125	0.88412	336.40	0.33313	0.0587
176.35	1.1073	0.89249	337.68	0.33466	0.0572
161.66	1.2193	0.90089	338.95	0.33630	0.0556
146.96	1.3538	0.90934	340.24	0.33806	0.0541
132.26	1.5184	0.91786	341.52	0.33997	0.0525
117.57	1.7242	0.92647	342.82	0.34208	0.0509
102.87	1.9890	0.93517	344.12	0.34441	0.0492
88.18	2.3424	0.94399	345.43	0.34706	0.0476
73.48	2.8375	0.95294	346.75	0.35013	0.0459
58.78	3.5807	0.96204	348.07	0.35382	0.0442
44.09	4.8202	0.97128	349.41	0.35846	0.0426
29.39	7.3003	0.98068	350.75	0.36487	0.0409
14.70	14.7430	0.99025	352.09	0.37558	0.0392
11.76	18.4648	0.99219	352.36	0.37899	0.0388
8.82	24.6679	0.99413	352.63	0.38336	0.0385
5.88	37.0744	0.99608	352.90	0.38949	0.0381
2.94	74.2944	0.99804	353.17	0.39992	0.0378

2350° F.

p	v^g	z	h^g	s^g	c_p^g
497.26	0.3348	0.73386	317.88	0.31470	0.0769
484.97	0.3462	0.74005	318.85	0.31532	0.0768
470.27	0.3608	0.74786	320.03	0.31608	0.0764
455.58	0.3765	0.75598	321.22	0.31686	0.0758
440.88	0.3933	0.76431	322.43	0.31767	0.0750
426.18	0.4114	0.77275	323.63	0.31848	0.0741
411.49	0.4307	0.78121	324.84	0.31932	0.0731
396.79	0.4515	0.78964	326.03	0.32017	0.0720
382.10	0.4738	0.79800	327.22	0.32104	0.0709
367.40	0.4979	0.80626	328.40	0.32193	0.0697
352.70	0.5239	0.81441	329.57	0.32284	0.0686
338.01	0.5520	0.82244	330.73	0.32378	0.0674
323.31	0.5827	0.83035	331.89	0.32474	0.0662
308.62	0.6161	0.83814	333.04	0.32573	0.0650
293.92	0.6529	0.84583	334.18	0.32675	0.0638
279.22	0.6934	0.85343	335.31	0.32780	0.0626
264.53	0.7384	0.86094	336.45	0.32890	0.0614
249.83	0.7886	0.86838	337.58	0.33004	0.0602
235.14	0.8450	0.87578	338.70	0.33123	0.0589
220.44	0.9089	0.88314	339.83	0.33248	0.0577
205.74	0.9819	0.89048	340.96	0.33380	0.0564
191.05	1.0662	0.89782	342.09	0.33519	0.0552
176.35	1.1645	0.90517	343.22	0.33667	0.0539
161.66	1.2807	0.91256	344.36	0.33826	0.0526
146.96	1.4202	0.92000	345.50	0.33997	0.0512
132.26	1.5909	0.92750	346.64	0.34183	0.0499
117.57	1.8044	0.93507	347.79	0.34388	0.0486
102.87	2.0791	0.94274	348.94	0.34616	0.0472
88.18	2.4456	0.95052	350.10	0.34875	0.0458
73.48	2.9591	0.95841	351.27	0.35177	0.0445
58.78	3.7298	0.96643	352.44	0.35540	0.0431
44.09	5.0151	0.97459	353.62	0.35999	0.0417
29.39	7.5868	0.98290	354.80	0.36634	0.0403
14.70	15.3043	0.99137	355.99	0.37700	0.0389
11.76	19.1635	0.99308	356.23	0.38039	0.0386
8.82	25.5955	0.99480	356.47	0.38475	0.0383
5.88	38.4599	0.99653	356.71	0.39087	0.0381
2.94	77.0535	0.99826	356.95	0.40129	0.0378

2450° F.

p	v^g	z	h^g	s^g	c_p^g
499.66	0.3593	0.76403	325.28	0.31724	0.0744
484.97	0.3735	0.77096	326.39	0.31796	0.0736

2450° F. cont.

p	v^g	z	h^g	s^g	c_p^g
470.27	0.3887	0.77811	327.50	0.31870	0.0728
411.49	0.4610	0.80748	331.92	0.32180	0.0686
396.79	0.4824	0.81478	333.01	0.32261	0.0675
382.10	0.5054	0.82201	334.08	0.32344	0.0664
455.58	0.4050	0.78539	328.61	0.31945	0.0718
440.88	0.4225	0.79275	329.72	0.32022	0.0708
426.18	0.4411	0.80012	330.82	0.32100	0.0697
367.40	0.5302	0.82916	335.15	0.32429	0.0653
352.70	0.5570	0.83621	336.21	0.32516	0.0642
338.01	0.5861	0.84317	337.26	0.32606	0.0631
323.31	0.6177	0.85004	338.30	0.32698	0.0620
308.62	0.6523	0.85682	339.33	0.32793	0.0609
293.92	0.6903	0.86353	340.36	0.32891	0.0599
279.22	0.7322	0.87017	341.38	0.32992	0.0588
264.53	0.7787	0.87675	342.40	0.33098	0.0577
249.83	0.8306	0.88328	343.41	0.33208	0.0567
235.14	0.8891	0.88978	344.42	0.33323	0.0556
220.44	0.9552	0.89626	345.44	0.33444	0.0545
205.74	1.0309	0.90273	846.45	0.33572	0.0534
191.05	1.1181	0.90921	347.46	0.33707	0.0523
176.35	1.2200	0.91571	348.47	0.33851	0.0512
161.66	1.3404	0.92225	349.49	0.34005	0.0501
146.96	1.4849	0.92883	350.50	0.34172	0.0490
132.26	1.6617	0.93548	351.53	0.34354	0.0479
117.57	1.8829	0.94220	352.55	0.34554	0.0468
102.87	2.1674	0.94901	353.58	0.34778	0.0456
88.18	2.5470	0.95591	354.62	0.35033	0.0445
73.48	3.0789	0.96293	355.66	0.35331	0.0434
58.78	3.8771	0.97007	356.70	0.35689	0.0422
44.09	5.2082	0.97733	357.75	0.36144	0.0410
29.39	7.8715	0.98474	358.81	0.36775	0.0399
14.70	15.8638	0.99229	359.87	0.37835	0.0387
11.76	19.8603	0.99382	360.09	0.38174	0.0385
8.82	26.5213	0.99536	360.30	0.38609	0.0383
5.88	39.8435	0.99690	360.51	0.39220	0.0380
2.94	79.8107	0.99845	360.73	0.40261	0.0378

2550° F.

p	v^g	z	h^g	s^g	c_p^g
499.66	0.3850	0.79161	332.52	0.31968	0.0703
484.97	0.3998	0.79782	333.54	0.32037	0.0694
470.27	0.4156	0.80414	334.56	0.32108	0.0684
455.58	0.4324	0.81052	335.57	0.32180	0.0674
440.88	0.4503	0.81692	336.58	0.32253	0.0664
426.18	0.4695	0.82331	337.57	0.32328	0.0654
411.49	0.4900	0.82968	338.56	0.32404	0.0644
396.79	0.5120	0.83599	339.54	0.32482	0.0634
382.10	0.5357	0.84225	340.52	0.32562	0.0624
367.40	0.5612	0.84844	341.48	0.32643	0.0614
352.70	0.5888	0.85457	342.43	0.32727	0.0604
338.01	0.6188	0.86062	343.38	0.32813	0.0594
323.31	0.6514	0.86661	344.32	0.32901	0.0585
308.62	0.6871	0.87254	345.25	0.32993	0.0575
293.92	0.7263	0.87841	346.17	0.33087	0.0566
279.22	0.7696	0.88424	347.10	0.33186	0.0556
264.53	0.8177	0.89003	348.01	0.33288	0.0547
249.83	0.8714	0.89579	348.93	0.33394	0.0538
235.14	0.9318	0.90153	349.84	0.33506	0.0529
220.44	1.0002	0.90726	350.75	0.33624	0.0519
205.74	1.0784	0.91300	351.66	0.33748	0.0510
191.05	1.1687	0.91875	352.57	0.33880	0.0501
176.35	1.2740	0.92453	353.49	0.34020	0.0491
161.66	1.3986	0.93035	354.40	0.34171	0.0482
146.96	1.5482	0.93622	355.32	0.34334	0.0473
132.26	1.7311	0.94215	356.23	0.34513	0.0463
117.57	1.9599	0.94816	357.16	0.34710	0.0454
102.87	2.2543	0.95424	358.08	0.34930	0.0444
88.18	2.6470	0.96042	359.01	0.35182	0.0435
73.48	3.1972	0.96671	359.95	0.35476	0.0425
58.78	4.0229	0.97311	360.89	0.35830	0.0415
44.09	5.3998	0.97963	361.83	0.36281	0.0406
29.39	8.1548	0.98628	362.78	0.36909	0.0396
14.70	16.4218	0.99307	363.74	0.37966	0.0386
11.76	20.5556	0.99444	363.93	0.38304	0.0384
8.82	27.4456	0.99582	364.12	0.38738	0.0382
5.88	41.2257	0.99721	364.32	0.39348	0.0380
2.94	82.5665	0.99860	364.51	0.40389	0.0378

ª Values are given to more significant figures than the data warrant in order to retain precision in differences.

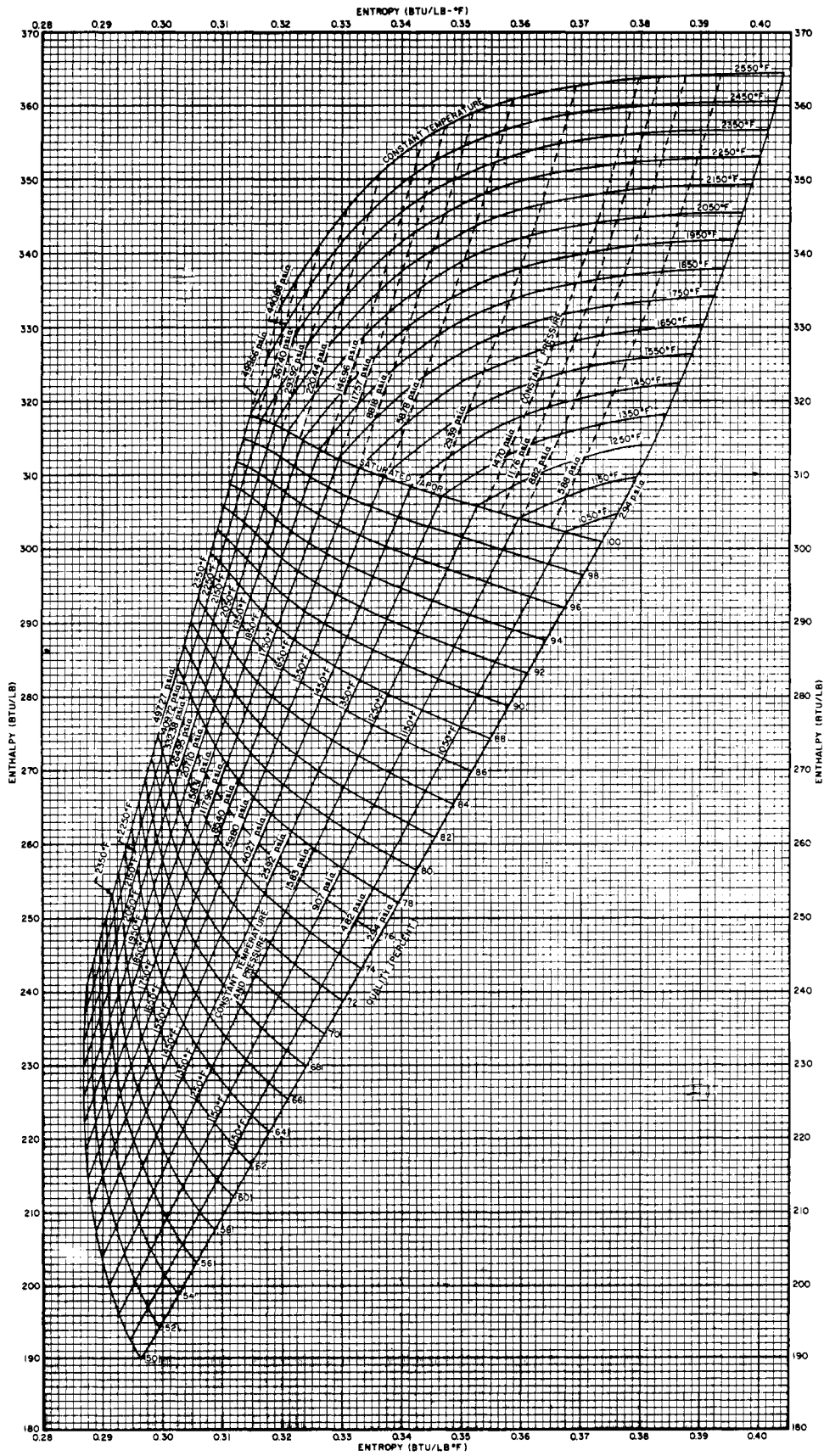agreement is good, as three of his points fall within 1.0% of the corresponding NRL values and the fourth within 3.0%.

The entropy of vaporization of each saturation point was obtained by dividing the appropriate enthalpy change by the absolute temperature.

Enthalpy and Entropy of Liquid Cesium. These properties of the saturated liquid at each temperature were obtained by substracting the enthalpy or entropy of vaporization from the corresponding property of the saturated vapor.

THERMODYNAMIC PROPERTIES OF CESIUM AND DISCUSSION

The saturation and superheat properties (1250° to 2550° F.) are presented in Tables II and III, and the thermal properties (1050° to 2550° F.) for both wet and dry vapors are presented graphically in a Mollier chart (Figure 3). The properties were computed from exact thermodynamic relationships involving the virial and vapor-pressure equations and are based on the properties of the ideal monomeric gas. The important virial equation was reduced from experimental PVT data covering a pressure range from 16.5 to 487.9 p.s.i.a. and a temperature range from 1305° to 2550° F. The vapor-pressure equation represents saturation data covering a range from 14.7 to 485.0 p.s.i.a. The experimental data, therefore, covers all states for which properties are reported except those with pressures below 16.5 p.s.i.a. Properties for these low-pressure states required short extrapolations of the virial and vapor-pressure equations and are of reduced accuracy.

Compressibility data and derived thermodynamic properties for cesium vapor at temperatures to 2060° F. were recently published by Tepper *et al.* (*13*). These properties may be compared directly to those generated in this study. If the NRL data are arbitrarily taken as reference and the property changes from p_s to 7.3 p.s.i.a. are compared at temperatures covering the overlapping range, the enthalpy changes reported by Tepper are 8% low, 32% high, and 350% high at temperatures of 1340°, 1700°, and 2060° F., respectively, and his entropy changes at the same temperatures are 8% low, 6% high, and 62% high. Although the observed discrepancies at lower temperatures in the two sets of properties can be explained by the random errors in Tepper's data (*13*), those at higher temperatures cannot be accounted for in this way. However, his values at higher temperatures appear to be completely out of line with existing spectroscopic information.

There are a number of publications in which thermodynamic properties of cesium vapor have been calculated by estimating gas imperfections from spectroscopic data. The properties generated in this article may be compared to those computed in recent publications by Agapova, Paskar, and Fokin (*2*) and Weatherford, Tyler, and Ku (*14*). If the NRL data are again taken as the reference and property changes from p_s to 2.9 p.s.i.a. are compared, the enthalpy changes reported by Agapova are 23 to 44% low and the entropy changes are 9% low. By a similar comparison, the enthalpy changes reported by Weatherford are 8 to 41% low and the entropy changes 4 to 8% low.

With the appearance of this article, thermodynamic properties based on experimental PVT data have now been published for three alkali metals—sodium, potassium, and cesium. The reported properties for each metal have been evaluated successfully for internal consistency and it is believed that they represent the best values available. They should be suitable for many calculations currently required for the design of systems using the metals as heat-transfer or working fluids. Even so, it is recognized that the reported properties can be evaluated better as additional properties are measured directly for the three metals. Particularly important would be reliable determina-

tions of the heat of vaporization and the specific heat of the liquid and vapor. A good example of this type of evaluation is provided by the recent measurements at Aerojet-General Nucleonics (*1*) of the heats of vaporization of cesium. These were measured directly and have been shown to substantiate those computed from the Calpeyron equation.

NOMENCLATURE

B = second virial coefficient, cu.ft. per mole
C = third virial coefficient, (cu.ft.)^2 per (mole)^2
D = fourth virial coefficient, (cu.ft.)^3 per (mole)^3
E = fifth virial coefficient, (cu.ft.)^4 per (mole)^4
c_p = specific heat at constant pressure, B.t.u. per lb.-° F.
f = free energy, B.t.u. per lb.
h = enthalpy per unit mass, B.t.u. per lb.
Δh_v = enthalpy change upon vaporization of a unit mass of equilibrium vapor, B.t.u. per lb.
ΔH_v = enthalpy change upon vaporization of a mole of equilibrium vapor, B.t.u. per lb.-mole
J = any unit conversion
M_1 = molecular weight of monomeric species
p = absolute pressure, lb. per sq. inch
R = gas constant
s = entropy per unit mass, B.t.u. per lb.-° F.
Δs_v = entropy change upon vaporization of a unit mass of equilibrium vapor, B.t.u. per lb.-° F.
T = absolute temperature, ° R.
t = temperature, ° F.
$\bar{V}$ = molal volume (per formula weight of monomer), cu.ft. per lb.-mole
v = specific volume, cu.ft. per lb.
z = compressibility factor, $p\bar{V}/RT$

Subscripts

0 = quantity at 0° R.
p = constant pressure change
s = quantity at saturation

Superscripts

g = quantity in gas state
l = quantity in liquid state
$°$ = standard state, 1 atm. for gas

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Salt Effects in Liquid-Liquid Equilibria

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The effect of lithium chloride, sodium chloride, and potassium chloride on the distribution of acetic acid, propionic acid, and butyric acid between benzene and water at 25° C. has been investigated. The method of Hand, originally developed for ternary systems, was used to correlate the distribution data for quaternary systems containing salt. A regression in two variables was used to express the slope and the intercept of the Eisen-Joffe Equation as linear functions of salt concentration. The order of decreasing salting out, on a weight basis, is

$$LiCl > NaCl > KCl$$

for all systems studied. On a mole basis, the effect of lithium chloride diminishes with increase in the number of carbon atoms in the carboxylic acid.

INVESTIGATIONS of salt effects in liquids have dealt primarily with the solubilities of nonelectrolytes, such as benzene, in water. Excellent summaries of this work appear in the literature (9, 11, 14). The effect of salts on the distribution of a solute between two immiscible solvents, a problem having engineering applications, has received very little attention.

There is general agreement on the physical phenomena responsible for the salt effects (1). The mathematical interpretation of these phenomena has resulted in several relationships which are, at best, semiquantitative. The limited applicability of these expressions emphasizes the complexity of the salt effects.

THEORIES OF THE SALT EFFECT

Three principal theories have been advanced to explain the salt effect. The hydration theory assumes that each salt ion binds a constant number of water molecules as a shell of oriented water dipoles surrounding the ion. This "bound" water is then unavailable as solvent for the nonelectrolyte. Considering the wide variation in hydration numbers reported in the literature, it appears that this concept permits only a qualitative estimate of the magnitude of the salt effect.

The electrostatic theory, which considers only the action of coulombic forces and omits other factors, was used by Debye and McAulay (7) to compute the partial free energy of a molecule relative to the pure solvent from the reversible electrical work. Because of simplifications and approximations made in its derivation, the Debye-McAulay equation is a limiting equation and can be regarded as a first approximation only. Butler (4), using a similarly simplified model, obtained an equation virtually identical with that of Debye and McAulay. Later Debye (6), taking into account the heterogeneity of the mixture of water and neutral solute, expressed the total free energy of the system, including the contribution due to the field of the ion, as a function of distance from the ion.

Since the electrostatic interaction between an ion and a neutral molecule is short range in nature, additional interaction terms of the London or van der Waals type must be considered more fully. These terms involve the polarizability of salt ions, solvent molecules, and nonelectrolyte solute molecules, as well as the special force fields originating from any component dipoles that may be present.

McDevit and Long (12), applying the "internal pressure" concept of Tammann (17) to nonpolar nonelectrolytes, calculated the free energy of transfer of the latter from pure water to the salt solution.

PREVIOUS WORK

The Setschenow equation (15)

$$\ln \frac{C^\circ}{C} = k_s X_s \tag{1}$$

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