Enthalpy and Heat Capacity of Solid and Liquid Lead

Recommendations

The recommended equations for the enthalpy and heat capacity of solid and liquid lead are from the assessment by Gurvich et al. [1] and are consistent with the thermodynamic values recommended by the Committee on Data for Science and Technology (CODATA) of the International Council of Scientific Unions [2]. Equations from the assessment by Gurvich et al. [1] are preferred to those given by the Scientific Group Thermodata Europe (SGTE) [3] because the SGTE equations are based on a 1962 assessment given in the JANAF Thermochemical Tables [4] that lacks data from measurements since 1962, which have been included in the more thorough, excellent Russian assessment [1].

Equations for enthalpy increments relative to the enthalpy of the solid at 298.15 K, in J mol^{-1} are:

Solid Phase (FCC):

$$H(s, T) - H(s, 298.15) = -7850.973 + 24.489T + 4.477 \times 10^{-3}T^2 + 4.520 \times 10^{4}T^{-1} \quad (1)$$

$$for \ 298\,K \le T \le 600.65\,K;$$

Liquid Phase:

$$H(l, T) - H(s, 298.15) = -7389.27 + 36.287T - 5.140 \times 10^{-3}T^2 + 3.158 \times 10^{5}T^{-1} + 1.371 \times 10^{-6}T^3 - 1.0875 \times 10^{-10}T^4 \quad (2)$$

$$for \ 600.65\,K \le T \le 3600\,K;$$

Equations, given by Gurvich et al. for the heat capacities of solid and liquid lead are:

Solid Phase (FCC):

$$C_P = +24.489 + 8.954 \times 10^{-3}T - 4.52 \times 10^{4}T^{-2} \quad (3)$$

$$for \ 298\,K \le T \le 600.65\,K;$$

Liquid Phase:

$$C_P = +36.287 - 10.280 \times 10^{-3}T - 3.158 \times 10^{5}T^{-2} + 4.113 \times 10^{-6}T^2 - 4.35 \times 10^{-10}T^3 \quad (4)$$

$$for \ 600.65\,K \le T \le 3600\,K;$$

Enthalpy increments in kJ mol^{-1} and heat capacities in J mol^{-1} K^{-1} that have been calculated from these equations are tabulated in Table 1 and shown in Figures 1 and 2. Table 2 gives enthalpy increments in kJ kg^{-1} and heat capacities in kJ kg^{-1} K^{-1} as a function of temperature. They were calculated using 207.2 g mol^{-1} for the atomic weight of lead.

Phase Transition Temperatures and Enthalpy Changes

The melting and normal boiling (vaporization) temperatures of lead are, respectively, 600.65 K and 2019.0 K. The triple point of lead, 600.65 K, is based on precise measurements of McLaren and Murdock [5]. Its uncertainty is given as 0.02 K [1]. The enthalpy of fusion, the difference between the solid and liquid enthalpy increments at the melting temperature, is 4.812 ± 0.040 kJ mol^{-1} [1]. The enthalpy of vaporization is 177.78 kJ mol^{-1}, the difference in the enthalpies of the liquid and ideal gas at the vaporization temperature, 2019 K. For the ideal gas, the thermodynamic functions recommended by CODATA are given in both the JANAF tables and book by Gurvich et al.

Uncertainties

Gurvich et al. give uncertainties for their tempered free energy function at a number of temperatures as well as uncertainties in the tabulated liquid enthalpy increments based on the inaccuracies in the thermodynamic functions. For solid lead, the corresponding uncertainty in enthalpies and heat capacities are less than 1%. Their uncertainties for liquid enthalpy increments are 0.4 k J mol^{-1} (1.6%) at 1000 K and 2.5 k J mol^{-1} (6%) at 1500 K. Comparison of the values for the enthalpy increments and heat capacities given by Gurvich et al. with those obtained from the SGTE equations and the JANAF tables shows that the enthalpy increments and solid heat capacities differ by less than 1%; the liquid heat capacities differ by 0.1% at the melting temperature and by 3% at 2000 K. Gurvich et al. have compared their recommendations with values from other assessments and found that the values for the enthalpy of liquid lead do not differ by more than 0.3 -0.5 J mol^{-1}.

Discussion

Gurvich et al [1] have made a very thorough review of the available data on the enthalpy and heat capacity of lead. They have evaluated the reliability of each set of data based on the experimental technique, the consistency of the data with values from other measurements, and analysis for

identification of systematic errors. Results of their assessment have been adopted by CODATA [2]. Their assessment differs from the JANAF assessment in their inclusion of the 1965 Sommelet [6] enthalpy data (571 - 1256 K) and the 1968 Leadbetter [7] heat capacity data (304-587 K) that were not available at the time of the JANAF assessment. Most early measurements were rejected by Guvich et al.[1] because these data were less accurate. However, Gurvich et al. included the enthalpy data of Bronson and Wilson [8] (203 - 393 K) along with data of Sommelet, Leadbetter, and Douglas and Dever [9] (373 - 1168 K) in their development of enthalpy and heat capacity equations for solid lead from 298.15 K to 600.65 K. Although the enthalpy of fusion, given in the JANAF tables is based only on the data of Douglas and Dever [9], enthalpy of fusion values from seven additional sources (four since the 1962 JANAF assessment) were evaluated by Gurvich et al.

From the melting point to 1256 K, the enthalpy and heat capacity of liquid lead recommended by Gurvich et al. are based on a combined analysis of the measurements of Douglas and Dever [9] (373 - 1168 K) and of Sommelet [6] (571 - 1256 K). At higher temperatures, the enthalpy was calculated from the assumption that the average heat capacity of liquid lead is 28.6 J mol^{-1} K^{-1} in the temperature range 1300 - 2000 K and then increases to 31.4 J mol^{-1} K^{-1} at 3500 K. This assumed behavior is based on the heat capacity behavior of liquid tin.

References

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Figure 1 Enthalpy Increments of Lead

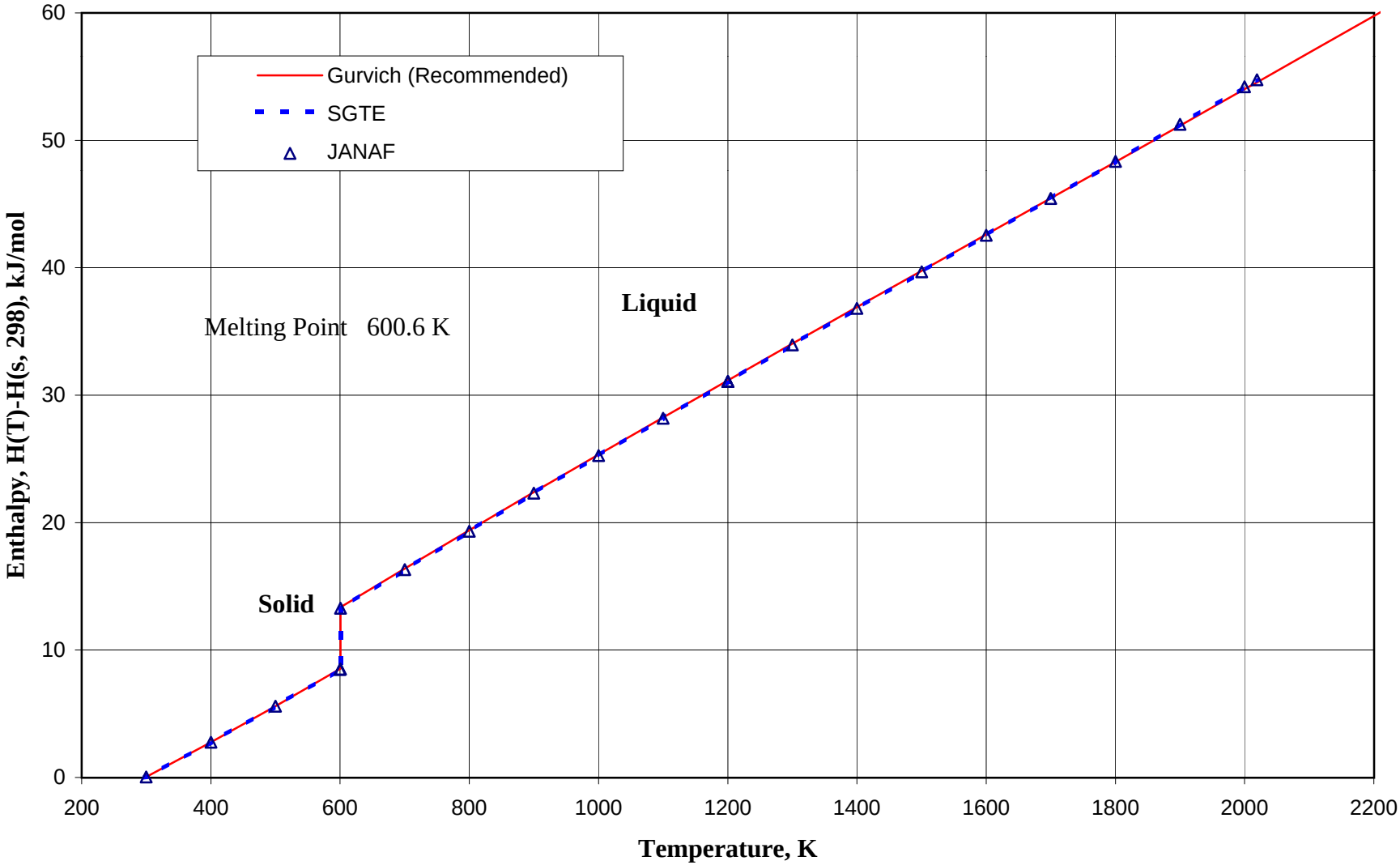

Figure 2 Heat Capacity of Lead

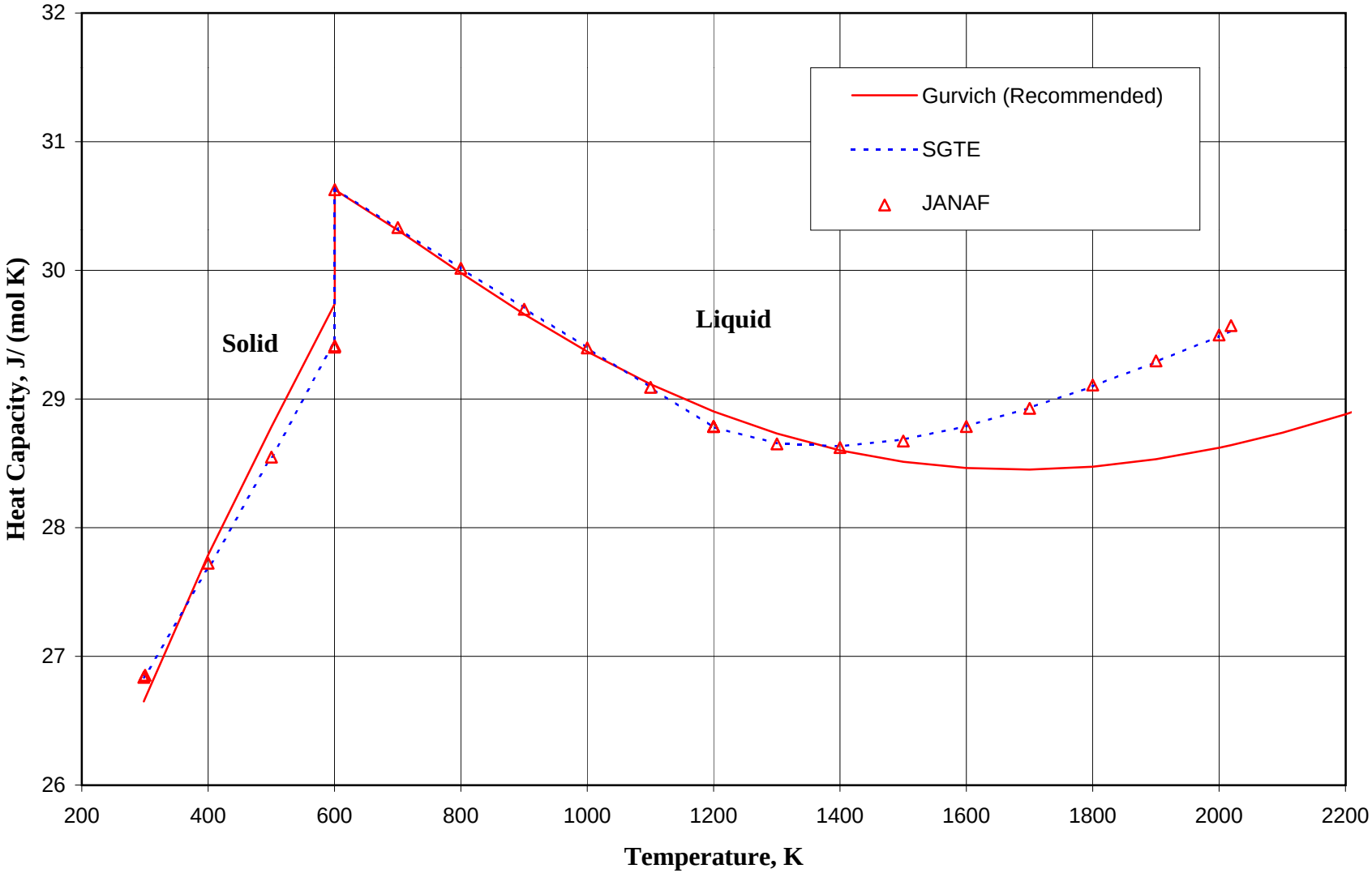

Table 1 Enthalpy and Heat Capacity of Solid and Liquid Lead per mole of Lead

Temperature K	H(T)-H(298.15 K) kJ mol^{-1}	Cp J mol^{-1} K^{-1}
298.15	0.0	26.65
300	0.05	26.67
400	2.77	27.79
500	5.60	28.79
600	8.53	29.74
600.65	8.55	29.74
600.65	13.36	30.63
700	16.39	30.31
800	19.40	29.98
900	22.38	29.66
1000	25.34	29.37
1100	28.26	29.12
1200	31.16	28.90
1300	34.04	28.73
1400	36.91	28.60
1500	39.76	28.51
1600	42.61	28.46
1700	45.46	28.45
1800	48.30	28.47
1900	51.15	28.53
2000	54.01	28.62
2019	54.56	28.64
2100	56.88	28.74
2200	59.76	28.88
2300	62.66	29.05
2400	65.57	29.24
2500	68.50	29.45
2600	71.46	29.67
2700	74.44	29.91
2800	77.44	30.16
2900	80.47	30.42
3000	83.53	30.68
3100	86.61	30.95
3200	89.72	31.22
3300	92.85	31.49
3400	96.01	31.76
3500	99.20	32.01
3600	102.42	32.26

Table 2 Enthalpy and Heat Capacity of Solid and Liquid Lead per kilogram

Temperature K	H(T)-H(298.15 K) kJ kg^{-1}	Cp kJ kg^{-1} K^{-1}
298.15	0.0	0.1286
300	0.2	0.1287
400	13.4	0.1341
500	27.0	0.1389
600	41.2	0.1435
600.65	41.3	0.1435
600.65	64.5	0.1478
700	79.1	0.1463
800	93.6	0.1447
900	108.0	0.1431
1000	122.3	0.1417
1100	136.4	0.1405
1200	150.4	0.1395
1300	164.3	0.1387
1400	178.1	0.1380
1500	191.9	0.1376
1600	205.7	0.1374
1700	219.4	0.1373
1800	233.1	0.1374
1900	246.9	0.1377
2000	260.7	0.1381
2019	263.3	0.1382
2100	274.5	0.1387
2200	288.4	0.1394
2300	302.4	0.1402
2400	316.5	0.1411
2500	330.6	0.1421
2600	344.9	0.1432
2700	359.3	0.1444
2800	373.8	0.1456
2900	388.4	0.1468
3000	403.1	0.1481
3100	418.0	0.1494
3200	433.0	0.1507
3300	448.1	0.1520
3400	463.4	0.1533
3500	478.8	0.1545
3600	494.3	0.1557