Calorimetric Study of Liquid Gold

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The enthalpy of liquid gold, in graphite crucibles, was determined in an adiabatic drop calorimeter between the melting point and 1806° K. Our data, which may be expressed as $H_T^\circ - H_{298.15}^\circ = -861.172 + 8.050\ T$ cal. per mole, were combined with those of other studies to compute revised thermodynamic functions. Liquid gold penetrated through crucibles fabricated from sintered tungsten rod.

MEASUREMENTS of the enthalpy of liquid gold were made to provide data to calculate more reliable thermodynamic functions for the metal than heretofore available. Such functions will be useful for the evaluation of gold vapor pressure data from various sources and will therefore aid in the selection of standard vapor pressure data for the metal.

When the work was started, only a few scattered measurements by Umino (*16*) and Wüst, Meuthen, and Durrer (*18*) were available. From these early data the heat capacity of liquid gold had been taken to be 7.0 cal./mole/° K. (*5*). While the work was in progress Plaza (*14*) reported eight more determinations of the enthalpy of the liquid to 1485° K. The present investigation extends the enthalpy measurements to 1800° K. Revised thermodynamic functions for gold are calculated by combining the present data for the liquid with those of Plaza and re-examining literature data for the heat capacity or enthalpy of the solid.

APPARATUS AND PROCEDURE

The measurements were made with a high temperature drop calorimeter having an adiabatic shielded receiver block designed and previously used by Levinson (*9, 11*). Samples are brought to temperature by means of a graphite tube heating element and are dropped into an adiabatic shielded copper block. Initial sample temperatures are read with an optical pyrometer. Levinson provides a complete description of the apparatus, operating procedure, and precision of the temperature control between the calorimeter block and the adiabatic shield.

The optical pyrometer was calibrated against a standard filament lamp to ±4° at 1100° C. Transmission corrections were made for a quartz window (0.94) and a prism (0.935) in the optical system.

MATERIALS AND CRUCIBLES

The gold used was 99.99% commercial metal. A slight surface film on the arc melted ingot was mechanically removed, and the remelted metal was vacuum-cast into the calorimeter crucibles.

Two materials were used to fabricate the calorimeter crucibles, which were 1½ inches high and 1 inch in diameter. Those machined from Poco graphite (Poco Graphite, Inc., Garland, Tex.) had ⅛-inch thick walls and those electromachined from a solid sintered tungsten rod had 1/16-inch thick walls. An internal web accommodated a black body hole whose ratio of length to diameter was greater than 10.

Tungsten proved to be an unsatisfactory crucible material. The first casting to load a crucible proceeded without incident. However, after a second casting to increase the amount of gold, leakage of gold through the crucible walls was observed. No structural defects had been detected by radiographic examination of the tungsten rod before machining or of the fabricated crucible. A 150× photomicrograph of a crucible section after failure is shown in Figure 1.

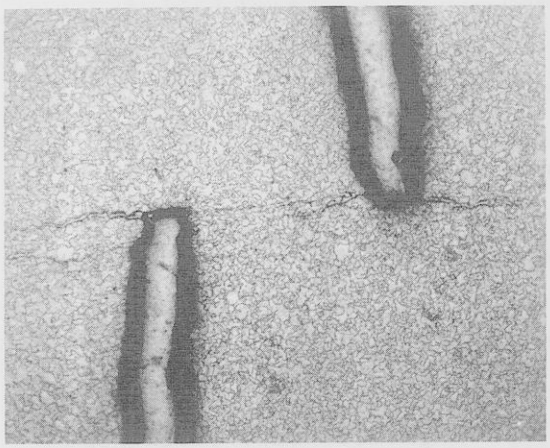

Figure 1. Gold penetration
150 X

The leakage cracks were radially distributed, suggesting that initially they were planes of residual stresses. Since no evidence of tungsten solubility was found by either microprobe or spectrographic analysis, these planes and the wetting of tungsten by gold appear to be conditions favorable for crack development.

Poco graphite is a fine-grained material which resisted liquid gold penetration and had good mechanical shock properties. Microscopic inspection and microprobe analysis of the crucible walls plus monitoring of crucible weight after each drop failed to provide evidence of diffusion through the crucible walls. Liquid metals have been found to diffuse through graphite from other sources (*3*).

To minimize crucible breakage, a ½-inch thick layer of graphite felt was placed in the bottom of the sample receiver hole in the copper block. Because the felt also acted as a thermal insulator, the time required to reach equilibrium in the block increased from around 30 minutes to about 60 or 80 minutes.

RESULTS AND DISCUSSION

Figure 2 gives the enthalpy data for graphite obtained by Levinson (*10*) and by the authors over the temperature range 1150° to 1850° K. from measurements on empty graph-

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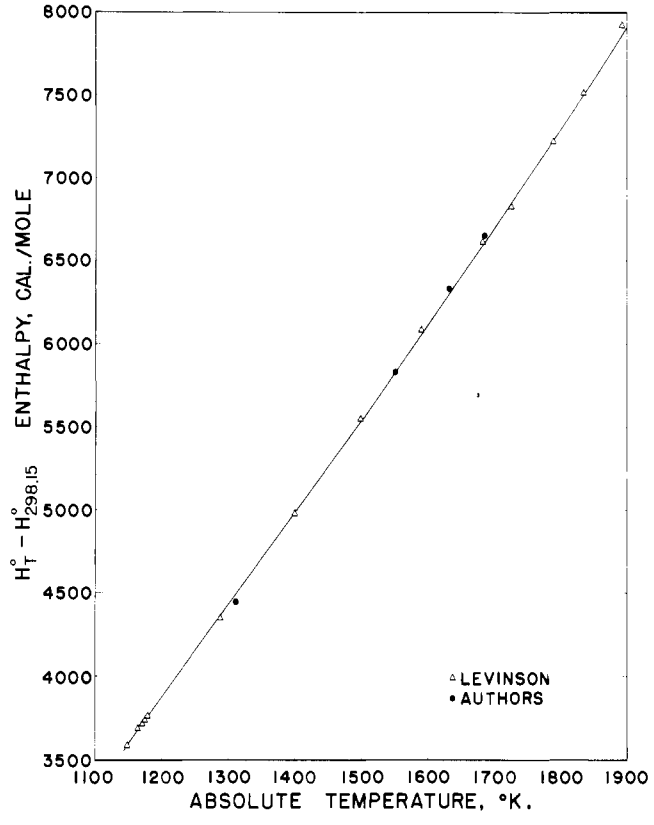

Figure 2. Enthalpy of crucible graphite

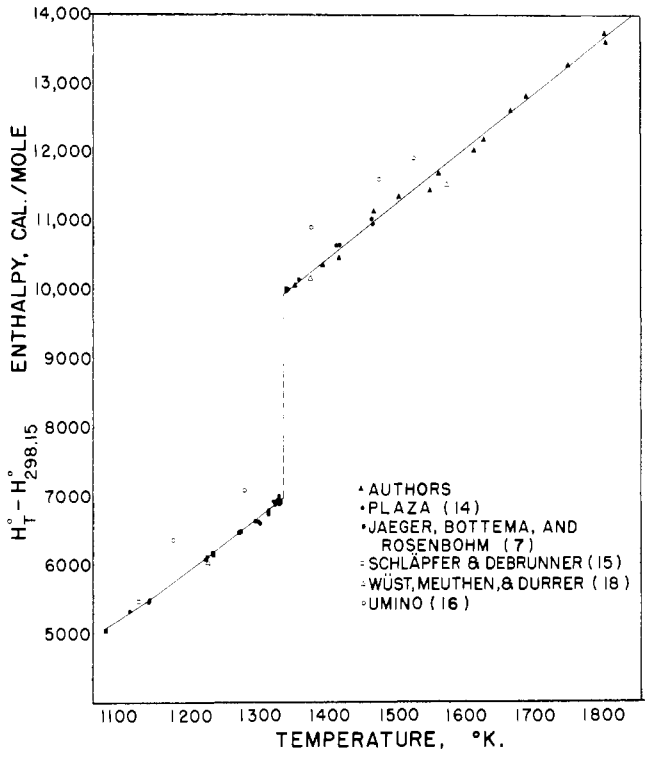

Figure 3. Enthalpy of gold

ite crucibles, without the graphite felt. The JANAF Thermochemical Tables (*8*) were used to correct the data from the final temperature of the copper block, approximately 310° K., to the standard state. An *F*-test (*12*) on variances of linear least squares fits of the data showed *F* to be significant for a quadratic equation but nonsignificant for a cubic equation (25% level of significance). The standard error of estimate for the following cubic fit was 18.4 cal. per mole.

$$H_T^\circ - H_{298.15}^\circ = 1136.5 - 2.199\ T + 0.00494\ T^2 - 1.007 \times 10^{-6}\ T^3 \text{ cal./mole (1150° to 1850° K.)} \quad (1)$$

Over the indicated temperature range, Equation 1 gives enthalpies which agree with those in the JANAF Thermochemical Tables to ±0.5% or less. This equation was used to determine the fraction of the total heat attributable to the crucible.

The experimental observations and the computed enthalpies of liquid gold are given in Table I. The gold contributes 30 to 40% of the total heat liberated to the copper block. The results were corrected from the final temperature of the copper block to the standard state with data from Hultgren *et al.* (*5*). The enthalpies are compared with results of other studies in Figure 3, which shows literature values for the enthalpy of the solid near the melting point from the data of Plaza (*14*), Jaeger, Bottema, and Rosembohm (*7*), Schläpfer and Debrunner (*15*), Umino (*16*), and Wüst, Meuthen, and Durrer (*18*).

From a least squares analysis of the liquid enthalpy data of the present study

$$H_T^\circ - H_{298.15}^\circ = -861.172 + 8.050\ T \text{ cal./mole (1336° to 1806° K.)} \quad (2)$$

$$C_p\text{Au(l)} = 8.050 \text{ cal./mole/° K.}$$

These enthalpy data have a standard error of estimate of ±109 cal. per mole. Part of the increase of the standard error of estimate with the gold-filled crucibles may be attributed to the increased time to equilibrium in the presence of the graphite felt. If the present data are combined with those of Plaza, a least squares fit gives

$$H_T^\circ - H_{298.15}^\circ = -699.74 + 7.953\ T \text{ cal./mole (1336° to 1806° K.)} \quad (3)$$

$$C_p\text{(l)} = 7.953 \text{ cal./mole/° K.}$$

for which the standard error of estimate is ±87 cal. per mole. A first degree equation was adequate to represent the data in both situations, as *F* was nonsignificant in both cases (25% level of significance). Equation 3 is used in the calculation of thermodynamic functions.

Table I. Experimental Data for Gold

Temperature, ° K. Sample T_i	Block T_f	Block ΔT	Gold Wt., Grams	Graphite Wt., Grams	$H_T^\circ - H_{298.15}^\circ$, Kcal./Mole
1806	310.889	7.933	78.4292	21.2669	13.602
1805	309.696	7.973	78.4292	21.3096	13.747
1751	310.180	6.743	82.2664	17.2925	13.277
1690	310.265	6.439	82.2664	17.3125	12.804
1667	310.304	7.136	78.4292	21.2411	12.609
1627	310.527	6.891	78.4292	21.2895	12.178
1613	310.376	6.007	82.2664	17.2800	12.021
1561	310.237	5.749	82.2664	17.2469	11.681
1549	310.303	6.412	78.4292	21.2961	11.423
1503	310.225	5.487	82.2664	17.3006	11.339
1463	310.322	5.294	82.2664	17.2451	11.134
1416	311.000	5.003	82.2664	17.3023	10.417
1392	310.156	5.531	78.4292	21.3107	10.343
1352	310.259	4.703	82.2664	17.2417	10.048

Calorimeter equivalent = 1947 + 1.2 T_f − 0.6 ΔT cal./deg. of temperature rise (*11*).

Table II. Selected Thermodynamic Functions for Gold

T, °K.	$-(G^\circ_T - H^\circ_{298.15})/T$, Cal./Mole/Deg.	$H^\circ_T - H^\circ_{298.15}$, Kcal./Mole	S°_T, Cal./Mole/Deg.	C°_p, Cal./Mole/Deg.
298.15	11.319 ± 0.059	0.0	11.319 ± 0.059	6.065
300	11.319	0.011	11.356	6.068
350	11.393	0.316	12.297	6.133
400	11.559	0.625	13.120	6.194
450	11.773	0.935	13.852	6.246
500	12.015	1.249	14.513	6.298
550	12.270	1.566	15.117	6.350
600	12.530	1.884	15.670	6.397
650	12.792	2.205	16.184	6.441
700	13.052	2.528	16.664	6.491
750	13.307	2.854	17.113	6.541
800	13.559	3.182	17.537	6.591
850	13.805	3.513	17.939	6.641
900	14.045	3.846	18.319	6.691
950	14.279	4.182	18.682	6.741
1000	14.509	4.521	19.030	6.791
1050	14.732	4.861	19.361	6.841
1100	14.949	5.205	19.681	6.891
1150	15.162	5.552	19.990	7.019
1200	15.369	5.908	20.292	7.222
1250	15.572	6.280	20.596	7.634
1300	15.772	6.670	20.903	8.007
1336(s)	15.913	6.964	21.125	8.300
1336(l)	15.913	9.925	23.342	7.953
1400	16.261	10.434	23.714	7.953
1500	16.776	11.230	24.263	7.953
1600	17.260	12.025	24.776	7.953
1800	18.148	13.616	25.713	7.953
2000	18.948	15.206	26.551	7.953
2200	19.674	16.800	27.309	7.953
2400	20.339	18.388	28.001	7.953
2600	20.953	19.978	28.637	7.953
2800	21.524	21.569	29.227	7.953
3000	22.056	23.159	29.775	7.953
3200	22.554	24.750	30.289	7.953
3400	23.024	26.340	30.771	7.953

$H^\circ_{298.15} - H^\circ_0 = 1434.8 \pm 6.6$ cal./mole.

THERMODYNAMIC FUNCTIONS

Thermodynamic function for Au (s,l) are tabulated in Table II. Functions for the solid are based on the sources listed by Hultgren *et al.* (*5*) plus the following additional sources: Martin (0.4° to 1.5° K., 3° to 30° K.) (*13*), du Chatenier and de Nobel (1° to 30° K.) (*1*), du Chatenier, de Nobel, and Boerstoel (1.3° to 30° K.) (*2*), Isaacs (1.5° to 4.2° K.) (*6*), Zimmerman and Crane (1.5° to 4.2° K.) (*19*), Will and Green (2° to 4° K.) (*17*), Franzosini and Clusius (12° to 273° K.) (*4*), and Plaza (404° to 1331° K.) (*14*). From the selected values of the thermodynamic functions of the solid and liquid the heat of fusion of gold is calculated to be 2961 cal. per mole at the defined melting point (IPTS) of gold, 1336° K. Hultgren *et al.* list 2955 cal. per mole for this quantity.

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Effect of Pressure and Temperature on Flammability Limits of Chlorinated Hydrocarbons in Oxygen-Nitrogen and Nitrogen Tetroxide–Nitrogen Atmospheres

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OF THE many halogenated hydrocarbons used as organic solvents, some are considered safer than others because they do not form flammable vapor-air mixtures at ordinary temperatures and pressure. For example, certain concentrations of methyl chloride and vinyl chloride vapors are flammable in air at atmospheric pressure and room temperature, whereas methylene chloride and trichloroethylene vapors are not flammable under the same conditions (*2*). However, many of the so-called "safe" halogenated solvents form flammable mixtures in air at elevated temperatures or reduced pressures where the fuel vapor pressure is not a limiting factor (*2, 7, 10, 13*). The flammability limits and burning velocities of such combustibles differ greatly from the values observed for their parent hydrocarbons (*1, 2, 6*); furthermore, the potential fire and explosion hazards are more serious in oxygen and nitrogen tetroxide atmospheres. However, flammability data in these atmospheres are meager for the halogenated hydrocarbons (*2, 9, 10*). Since this information is of interest in rocket and space flight applications, the current investigation was undertaken.

Lower and upper limits of flammability were determined