Table VII. Empirical Constants *a* and *b* for the Ternary System Correlation

The Binary System Plus	*a*	*b*
Hexylene glycol	0.210	−0.170
Aniline	0.580	−0.370
Furfural	0.433	−0.484

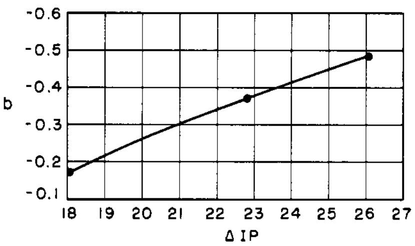

Figure 13. Empirical constant "b" is a function of internal pressure difference between solvent and 2,4-DMP

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Heat Content of Platinum

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CHEMICAL INERTNESS, high melting point, and freedom from allotropic and magnetic transformations give platinum obvious advantages as a secondary standard for calibrating high-temperature calorimeters. However, currently accepted tables (*8, 13*) of the heat content of platinum can be criticized because the values below 500° K. are too high to join smoothly with reliable low-temperature (< 298° K.) heat capacity data (*1, 12*), and because the tables are based mainly on the drop calorimetry of Jaeger and others (*4, 5, 6*) in which, as Oriani (*10*) has pointed out, the heat lost by the sample during the drop was not properly taken into account.

The performance of a diphenyl ether calorimeter used in this laboratory is routinely checked by dropping samples of platinum. The results so obtained scatter considerably more than those by Jaeger and others (*4, 5, 6*) from larger samples, but they do show clearly that the over-all systematic error in Jaeger's work is very small. They also show the previously tabulated heat contents at 400° and 500° K. are somewhat too high.

EXPERIMENTAL

Since the diphenyl ether calorimeter has been described previously (*3*), the procedure and sample preparation will be described here only briefly.

Four samples, each about 99.99% pure, were used in the determinations. The first was a solid sphere about 8 mm. in diameter weighing 5.6 grams. The second was formed from 0.7 gram of 0.127 mm. platinum foil to make a hollow sphere of the same diameter as the first. The third and fourth samples were similar to the second, except that they were filled with 1.9 grams of platinum wire and 1.1 grams of platinum foil, respectively.

The samples were heated under an argon atmosphere in a resistance furnace to a measured temperature, *T*, then dropped into the diphenyl ether calorimeter. The heat liberated by a sample within the calorimeter is absorbed by a mixture of liquid plus solid diphenyl ether, melting some of the solid without changing its temperature. The expansion accompanying melting forces mercury from a pool in the bottom of the diphenyl ether chamber out into a calibrated horizontal capillary tube. The heat given up by the sample within the calorimeter can be found by multiplying the weight of mercury displaced by the factor 18.91 cal./gram Hg determined by Jessup (7) at the National Bureau of Standards. To obtain the heat content of the sample at temperature T, one must add a quantity δ representing the heat lost during the drop from furnace to calorimeter. If q_1 and q_2 correspond to the heat effects observed when two samples containing m_1 and m_2 g-atoms of platinum are dropped from the same initial temperature, T, then the heat content per gram atom relative to 300° K., the melting point of diphenyl ether, will be

$$H_T - H_{300} = \frac{q_1 + \delta_1}{m_1} = \frac{q_2 + \delta_2}{m_2}$$

For samples of the same size, shape, and emissivity, $\delta_1 = \delta_2$, so that δ can be determined by measurement of the heat and mass of two of the four samples described. An analysis of many measurements has yielded a set of δ-values (Figure 1) which is consistent with the results from all four samples.

The experimental results referred to 298.15° K. are given in Table I and plotted in terms of the function $(H^0_T - H^0_{298.15})/(T - 298.15)$ in Figure 2 with the results of Jaeger and others (4, 5, 6) and White (14). The scatter of present results ($\pm 0.5\%$) is greater than that of the more precise measurements of Jaeger and others ($\pm 0.1\%$) and White

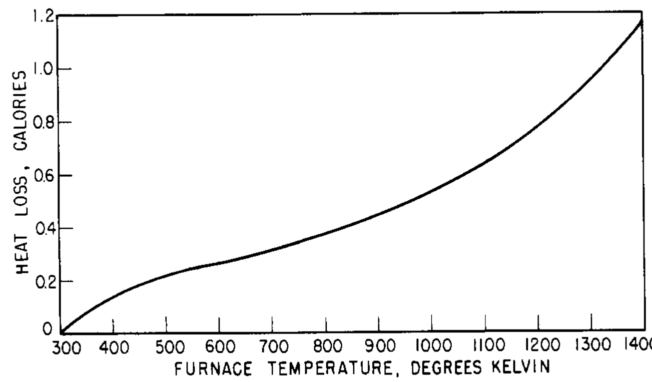

Figure 1. Heat loss of specimens during drop

Table I. Experimental Results

(Platinum Sphere)

T, °K.	$H^0_T - H^0_{298.15}$, Cal./G. Atom	T, °K.	$H^0_T - H^0_{298.15}$, Cal./G. Atom
339.1	253	600.5	1933
343.8	282	658.6	2319
344.5	286	658.6	2322
344.6	286	675.0	2426
345.8	296	682.0	2468
346.3	298	687.4	2504
346.5	299	688.4	2507
351.5	331	701.8	2598
351.8	334	705.3	2629
358.6	375	717.1	2704
366.8	429	782.3	3155
380.5	514	797.3	3259
384.8	537	799.9	3263
386.7	553	803.9	3276
388.4	560	804.0	3304
396.7	615	822.4	3415
397.1	614	832.1	3462
400.3	636	861.2	3681
400.6	642	875.0	3784
400.8	639	878.0	3801
403.8	656	894.9	3923
403.9	659	895.3	3924
405.5	671	895.4	3923
415.4	731	902.7	3963
448.7	940	907.0	3986
452.6	973	909.7	4012
457.6	994	949.2	4294
483.0	1157	961.8	4377
483.9	1164	973.3	4466
484.8	1175	981.6	4526
487.2	1186	988.5	4572
487.2	1191	989.3	4581
490.1	1213	990.2	4586
492.3	1222	997.3	4619
494.7	1230	1026.4	4859
496.6	1253	1030.5	4869
499.7	1275	1063.8	5107
503.8	1301	1106.0	5419
505.3	1312	1113.9	5500
505.6	1315	1208.0	6143
576.8	1767	1294.1	6828
577.0	1776	1295.5	6775
586.9	1848	1296.6	6794
593.1	1884	1389.0	7553
593.6	1889	1391.2	7512
595.9	1903	1403.8	7634
598.1	1913		

(Platinum Wire Sample)

T, °K.	$H^0_T - H^0_{298.15}$, Cal./G. Atom	T, °K.	$H^0_T - H^0_{298.15}$, Cal./G. Atom
500.5	1277	910.7	4039
512.4	1366	989.5	4575
518.9	1389	989.5	4603
520.1	1400	991.3	4566
596.1	1900	998.0	4656
597.8	1908	1001.3	4649
599.5	1923	1005.7	4701
602.9	1937	1035.0	4888
620.2	2070	1101.8	5399
631.9	2123	1105.8	5451
633.1	2129	1107.5	5431
638.3	2166	1163.5	5863
682.3	2473	1174.9	5925
688.0	2511	1186.2	6012
698.0	2589	1191.0	6023
719.0	2722	1192.1	6017
794.7	3237	1202.0	6134
796.7	3257	1208.5	6165
798.5	3263	1291.7	6765
819.6	3425	1297.8	6819
826.7	3422	1298.0	6807
888.5	3894	1395.2	7508
888.6	3886	1397.3	7623
892.7	3912	1428.6	7791
894.2	3921	1434.5	7836
895.7	3936	1435.0	7839

(Platinum Foil Sample)

T, °K.	$H^0_T - H^0_{298.15}$, Cal./G. Atom	T, °K.	$H^0_T - H^0_{298.15}$, Cal./G. Atom
503.0	1301	1093.1	5356
584.2	1840	1093.5	5372
669.5	2394	1094.0	5333
691.2	2537	1095.3	5380
757.5	2981	1160.4	5815
797.4	3261	1189.3	6039
804.7	3293	1193.7	6075
879.2	3832	1194.4	6066
894.2	3938	1198.6	6123
897.9	3967	1209.5	6195
905.1	3979	1284.4	6752
905.6	3967	1296.0	6826
949.5	4325	1296.3	6772
989.9	4573	1300.5	6874
997.5	4629	1306.0	6866
999.1	4627	1375.9	7405
1020.6	4819	1377.8	7375
1022.6	4812	1380.2	7440
1045.2	5002	1382.0	7434
1071.9	5150	1393.7	7472
1078.8	5228	1409.7	7548

(±0.3%). They therefore contribute nothing to the precision of the values. They do show, however, that there is no important systematic error in the work of Jaeger and others such as would occur from significant uncompensated losses of heat during the drop of the samples. They also show that the tabulated values of Kelley (*8*) and Stull and Sinke (*13*) at 400° and 500° K. are too high and thus make reasonable a choice of new values at these temperatures which agree with low temperature C_p data (*1*, *12*). C_p is molal heat capacity at constant pressure.

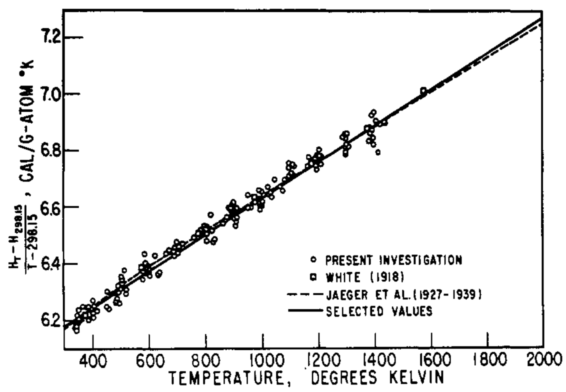

Figure 2. Heat content of platinum expressed in terms of the function $(H_T - H_{298.15})/T - 298.15)$

DISCUSSION

The three sets of heat content measurements (Figure 2) can be fitted within 0.2% by the analytical expression

$$H^0_T - H^0_{298.15} = 0.0006425\ T^2 + 5.796\ T - 1785$$

which is shown as a solid line. Although the data are somewhat more closely fitted by the two equations (Figure 2) which Jaeger and others (*4*, *5*, *6*) use to describe their results, the scatter in existing data would not seem to warrant such a refined description. The thermodynamic properties of platinum given in Table II have been calculated from the above equation and are considered to be accurate within 0.3%. Measurements reported prior to 1918 seemed too unreliable to warrant any weight in the final selection. The heat content data of Esser, Averdieck, and Grass (*2*) were rejected because their sample was contaminated with iridium. C_p measurements of Persoz (*11*) on a sample of unstated purity were also rejected as being too low.

It is encouraging that the new selection joins smoothly in both C_p and (dC_p/dT) with the extrapolated low-temperature measurements of Simon and Zeidler (*12*) and Clusius, Losa, and Franzosini (*1*). The values given in Table II are thought to be both more reliable and more self-consistent than those of previous tabulations (*8*, *13*). Values of the free energy function are based on $S^0_{298.15}$ = 9.95 ± 0.05 as given by Kelley and King (*9*).

Table II. Thermodynamic Values for Platinum

		Cal./Deg. G. Atom		
T, ° K.	$H^0_T - H^0_{298.15}$ Cal./G. Atom	C_p	$S^0_T - S^0_{298.15}$	$-(F^0_T - H^0_{298.15})/T$
298.15	0	6.18	0.00	9.95
300	11	6.18	0.04	9.95
400	636	6.31	1.83	10.19
500	1275	6.44	3.26	10.66
600	1925	6.57	4.44	11.18
700	2590	6.70	5.46	11.72
800	3260	6.82	6.37	12.24
900	3950	6.95	7.18	12.74
1000	4650	7.08	7.92	13.21
1100	5370	7.21	8.60	13.67
1200	6100	7.34	9.23	14.10
1300	6840	7.47	9.82	14.51
1400	7590	7.60	10.38	14.91
1500	8350	7.72	10.91	15.29
1600	9130	7.85	11.41	15.65
1700	9920	7.98	11.89	16.00
1800	10730	8.11	12.35	16.34
1900	11550	8.24	12.79	16.66
2000	12380	8.37	13.22	16.98
2043	12740	8.42	13.40	17.11

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