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THE THERMODYNAMIC PROPERTIES OF RHENIUM ON ITS-90

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Rhenium exists in a close-packed hexagonal structure with lattice parameters at 293 K of a = 0.27610 nm c = 0.44583 nm and a density of 21.01 g cm^{-3} (Donohue [1] corrected for conversion factors recommended in the 1986 revision of the fundamental constants [2]). Wherever possible values have been corrected to the currently accepted atomic weight of 186.207 [3] and to the revision of the ITS-90 temperature scale [4,5]. The melting point determined by Sims, Craighead and Jaffee [6] corrects to 3458 ± 20 K on this scale. A superconducting transition temperature (T_c) of 1.700 K takes in to account the recommended values of both Roberts [7] and Hultgren et al [8]. The previous review of the thermodynamic properties was by the latter authors.

SOLID

Below 4 K the specific heat in the normal state can be represented as

$$D/T^2 + \gamma T + 1943.73 (T/\Theta_D)^3 \text{ J mol}^{-1} \text{ K}^{-1}$$

where D is the nuclear quadrupole coefficient, γ is the electronic coefficient and Θ_D is the limiting Debye temperature.

	D (mJ K mol^{-1})	γ (mJ mol^{-1} K^{-2})	Θ_D (K)
Keesom and Bryant [9] 0.37-4.2 K	0.052 ± 0.002	2.31 ± 0.02	417 ± 10
Blanpain [10] 1.2-24 K	---	2.26 ± 0.03	407 ± 10
Smith and Keesom [11] 0.16-3.6 K	0.049 ± 0.002	2.29 ± 0.02	416 ± 10
Batt et al [12] 0.3-3 K	---	2.22	---
Rockwood, Gregory and Goodstein [13] 0.1-0.5 K	0.061	----	---
Gregers-Hansen, Krusius and Pickett [14] 0.02-0.3 K	0.0406 ± 0.0006 a	----	---
Buttet and Baily [15]	0.0459 b	----	---
RECOMMENDED	0.049	2.29	416

a. Gregers-Hansen et al obtained a second nuclear term 3.4E-5/T^3 mJ K^2 mol^{-1}
b. Determined using nuclear acoustic resonance (all other values were based on specific heat measurements).

The selected values are based mainly on the specific heat measurements of Smith and Keesom. In addition Shepard and Smith [16] determined Θ_D to be 416 K from elastic constant measurements whilst similar measurements of Fisher and Dever [17] lead to 406 K. The measurements of Keesom and Bryant are 2% higher initially but converge to the selected values. Similarly the measurements of Blanpain are initially

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1% low but converge to the selected values above 4 K.

In the superconducting state selected values are based on the measurements of Smith and Keesom with those of Blanpain being 3 to 7% lower.

In agreement with Hultgren et al [8] selected values in the range 10 to 270 K are based on the specific heat measurements of Piesbergen [18] 11-272 K which are preferred to those of Smith, Oliver and Cobble [19] 20-300 K. The latter measurements scatter about the selected values below 100 K but then average 3% higher above this temperature. Measurements of Horowitz and Daunt [20] 68-77 K scatter 8% high to 5% low about the selected curve.

Above 270 K selected values are based on the enthalpy measurements of Conway and Hein [21] 1264-2644 K, as reported by Hoch [22], and those of Lin and Frohberg [23] 2913-3734 K which are joined smoothly with the low temperature data using the following equation which has an overall accuracy of 0.6% (± 340 J mol^{-1}):

$$H^\circ_T - H^\circ_{298.15} = 23.7544\ T + 3.47270E\text{-}3\ T^2 - 1.06132E\text{-}6\ T^3 + 1.80731E\text{-}10\ T^4 + 48512.6/T - 7527.09 \quad J\ mol^{-1}$$

However the measurements of Conway and Hein were not used above 2000 K since above this temperature they deviate up to 4% high. Enthalpy measurements of Jaeger and Rosenbohm [24] 667-1474 K are 1 to 3% higher than the selected values. Specific heat measurements of Arutyunov and Filippov [25] 1100-2400 K as revised by Filippov [26] 1100-2500 are 6 to 11% high, those of Taylor and Finch [27] 300-3120 K are on average 2% high up to 2000 K and then increase sharply to 54% high. The two measurements of Lehman [28] 860-1400 K are 5% low and 6% high respectively whilst the measurements of Rudkin, Parker and Jenkins [29] 1410-2720 K are 15% low to 12% high and the measurements of Sims et al [30] 1400-2600 K are extraordinarily 89 to 112% high.

There have been a number of determinations of enthalpy using the rapid pulse heating technique. At the melting point the enthalpy value of Dolomanov et al [31] (determination at the melting point only) is 4% higher than the selected value. The measurements of Hixson and Winkler [32] 2427-5725 K are from 6 to 17% higher than the selected enthalpy curve whilst those of Thévenin et al [33] 1817-6951 K are from 7 to 14% higher.

LIQUID

After correction to the accepted melting point the liquid enthalpy measurements of Lin and Frohberg [23] 2913-3734 K can be represented by the following equation which has an overall accuracy of 1.1% (± 1720 J mol^{-1}):

$$H^\circ_T - H^\circ_{298.15} = 49.519\ T - 39050 \quad J\ mol^{-1}$$

leading to a constant liquid specific heat of 49.5 ± 5.8 J mol^{-1} K^{-1}, an heat of fusion of 34.1 ± 1.8 kJ mol^{-1} and an entropy of fusion of 9.85 ± 0.51 J mol^{-1} K^{-1}. The following values have been obtained by the rapid pulse heating technique:-

	Enthalpy of Liquid at mpt	Heat of Fusion kJ mol^{-1}	Liquid Cp J mol^{-1} K^{-1}
Pottlacher, Neger and Jäger [34,35] mpt to 7500 K	- 6%	—	46.6
Dolomanov et al [31] melting point only	+ 2%	33.5	—
Hixson and Winkler [32] 2427-5725 K	+ 8%	28.5	49.7
Thévenin et al [33] 1817-6951 K	+ 4%	29.4	43.4

GAS

Thermodynamic properties of the monatomic gas were calculated from 289 energy levels, mainly those listed by Klinkenberg et al [36] but including the revision and extension by Wyart [37], using the method outlined by Kolsky, Gilmer and Gilles [38] together with the 1986 fundamental constants [2] except for the Gas Constant and the Boltzmann Constant which are based on the later measurements of Moldover et al [39]. Values were corrected to the standard state pressure of one bar [40].

VAPOUR PRESSURE

Third law heats of sublimation were calculated from the following Langmuir free-evaporation determinations:

Authors	Range (K)	$\Delta H^{\circ}_{298.15}$ (kJ mol^{-1})
Blackburn [41]	2697-2909	778.0 ± 2.5 a
Strassmair and Stark [42]	2664-3195	774.7 ± 0.7
Sherwood et al [43]	2497-3003	783.6 ± 2.9
Plante and Szwarc [44]	2445-2732	783.3 ± 0.6 b
RECOMMENDED		780 ± 6

NOTES: a Trend with temperature
b Series IV only, series I to III 2351-3062 K were rejected by the authors

In agreement with Hultgren et al [8] the recommended value is based on an average of the last three determinations. In addition second law heats of sublimation of 761 ± 39 kJ mol^{-1} and 785 ± 19 kJ mol^{-1} are obtained from the mass spectrometric measurements of Zandberg, Ionov and Tontegode [45] 2400-2750 K and Sasaki, Kubo and Asano [46] 2590-2780 K respectively.

PHYSICAL CONSTANTS

Velocity of light =	299 792 458 m s^{-1} [2]
Avogadro's Number =	6.0221367 (36) E+23 mol^{-1} [2]
Planck's Constant =	6.6260755 (40) E-34 J s [2]
Gas Constant =	8.314471 (14) J mol^{-1} K^{-1} [39]
Boltzmann Constant =	1.3806513 (25) E-23 J K^{-1} [39]

LOW TEMPERATURE SPECIFIC HEAT DATA

T K	C°p J mol^{-1} K^{-1}		T K	C°p J mol^{-1} K^{-1}	T K	C°p J mol^{-1} K^{-1}
0.2	0.00123 *	0.00168 **	8	0.0328	70	13.031
0.4	0.000384 *	0.00122 **	9	0.0413	80	14.956
0.6	0.000698 *	0.00152 **	10	0.0531	90	16.541
0.8	0.00162 *	0.00192 **	12	0.0907	100	17.862
1.0	0.00288 *	0.00237 **	14	0.149	120	19.826
1.2	0.00457 *	0.00283 **	16	0.233	140	21.212
1.4	0.00642 *	0.00331 **	18	0.353	160	22.218
1.6	0.00841 *	0.00379 **	20	0.518	180	22.924
1.700	0.00946 *	0.00404 **	25	1.180	200	23.502
2	0.00481		30	2.210	220	23.971
3	0.00760		35	3.513	240	24.345
4	0.0109		40	4.967	260	24.633
5	0.0149		45	6.468	280	24.847
6	0.0198		50	7.946	298.15	25.016
7	0.0257		60	10.685		

* Superconductor ; ** Non-superconductor (in magnetic field)

	SOLID	GAS
$H^\circ_{298.15}-H^\circ_0$ J mol^{-1}	5333	6197.4
$S^\circ_{298.15}$ J mol^{-1} K^{-1}	36.48 *	188.941

* Does not include nuclear contribution

Corrected to one bar standard state pressure

GIBBS FREE ENERGY EQUATIONS

SOLID 298.15-3458 K

$$G^\circ_T-H^\circ_{298.15} = -23.7544\ T\ln(T) + 124.8239\ T - 3.47270E\text{-}3\ T^2 + 5.30660E\text{-}7\ T^3 - 6.02437E\text{-}11\ T^4 + 24256.3/T - 7527.09\ \text{J mol}^{-1}$$

LIQUID 3458-6000 K

$$G^\circ_T-H^\circ_{298.15} = -49.519\ T\ln(T) + 335.72915\ T - 39050\ \text{J mol}^{-1}$$

HIGH TEMPERATURE DATA

CONDENSED PHASES Re(s,l)

T K	C°p J mol⁻¹ K⁻¹	$H°_T-H°_{298.15}$ J mol⁻¹	S° J mol⁻¹ K⁻¹	$-(G°_T-H°_{298.15})/T$ J mol⁻¹ K⁻¹
298.15	25.016	0	36.482	36.482
300	25.032	46	36.637	36.482
400	25.766	2588	43.945	37.474
500	26.327	5194	49.757	39.369
600	26.797	7851	54.599	41.515
700	27.205	10551	58.761	43.688
800	27.567	13290	62.418	45.805
900	27.893	16064	65.684	47.836
1000	28.190	18868	68.639	49.771
1100	28.464	21701	71.339	51.611
1200	28.720	24560	73.826	53.360
1300	28.962	27444	76.135	55.024
1400	29.196	30352	78.290	56.609
1500	29.427	33283	80.312	58.123
1600	29.658	36238	82.218	59.570
1700	29.895	39215	84.023	60.956
1800	30.141	42217	85.739	62.285
1900	30.402	45244	87.376	63.563
2000	30.681	48298	88.942	64.793
2100	30.982	51381	90.446	65.979
2200	31.312	54495	91.895	67.124
2300	31.672	57644	93.295	68.232
2400	32.069	60831	94.651	69.305
2500	32.506	64059	95.969	70.345
2600	32.988	67334	97.253	71.355
2700	33.519	70659	98.508	72.338
2800	34.103	74039	99.737	73.294
2900	34.745	77481	100.945	74.227
3000	35.449	80990	102.134	75.138
3100	36.219	84573	103.309	76.027
3200	37.060	88236	104.472	76.898
3300	37.976	91987	105.626	77.751
3400	38.972	95834	106.775	78.588
3458(s)	39.587	98112	107.439	79.066
3458(l)	49.519	132187	117.293	79.066
3500	49.519	134267	117.891	79.529
3600	49.519	139218	119.286	80.614
3700	49.519	144170	120.642	81.677
3800	49.519	149122	121.963	82.720
3900	49.519	154074	123.249	83.743
4000	49.519	159026	124.503	84.746
4100	49.519	163978	125.726	85.731
4200	49.519	168930	126.919	86.698
4300	49.519	173882	128.084	87.647
4400	49.519	178834	129.223	88.579
4500	49.519	183786	130.335	89.494
4600	49.519	188737	131.424	90.394
4700	49.519	193689	132.489	91.278
4800	49.519	198641	133.531	92.148
4900	49.519	203593	134.552	93.003
5000	49.519	208545	135.553	93.844
5100	49.519	213497	136.533	94.671
5200	49.519	218449	137.495	95.486
5300	49.519	223401	138.438	96.287
5400	49.519	228353	139.364	97.076
5500	49.519	233305	140.272	97.853
5600	49.519	238256	141.165	98.619
5700	49.519	243208	142.041	99.373
5800	49.519	248160	142.902	100.116
5900	49.519	253112	143.749	100.848
6000	49.519	258064	144.581	101.570

HIGH TEMPERATURE DATA

GAS PHASE Re(g,bar)

T K	C°p J mol^{-1} K^{-1}	H°$_T$−H°$_{298.15}$ J mol^{-1}	S° J mol^{-1} K^{-1}	−(G°$_T$−H°$_{298.15}$)/T J mol^{-1} K^{-1}
298.15	20.786	0	188.941	188.941
300	20.786	38	189.069	188.941
400	20.786	2117	195.049	189.757
500	20.786	4196	199.688	191.296
600	20.786	6274	203.477	193.020
700	20.786	8353	206.681	194.749
800	20.786	10432	209.457	196.418
900	20.786	12510	211.905	198.005
1000	20.787	14589	214.095	199.507
1100	20.787	16667	216.077	200.924
1200	20.790	18746	217.885	202.264
1300	20.796	20826	219.550	203.530
1400	20.809	22906	221.091	204.730
1500	20.833	24988	222.528	205.869
1600	20.873	27073	223.874	206.953
1700	20.934	29163	225.141	207.986
1800	21.025	31261	226.340	208.972
1900	21.152	33369	227.480	209.917
2000	21.324	35493	228.569	210.822
2100	21.547	37636	229.614	211.692
2200	21.828	39804	230.623	212.530
2300	22.175	42004	231.601	213.338
2400	22.591	44241	232.553	214.119
2500	23.081	46524	233.485	214.875
2600	23.648	48860	234.401	215.608
2700	24.294	51257	235.305	216.321
2800	25.020	53722	236.202	217.015
2900	25.824	56263	237.093	217.692
3000	26.704	58889	237.983	218.354
3100	27.657	61606	238.874	219.001
3200	28.678	64423	239.768	219.636
3300	29.761	67344	240.667	220.260
3400	30.900	70377	241.573	220.874
3458	31.583	72189	242.101	221.225
3500	32.087	73526	242.485	221.478
3600	33.313	76795	243.406	222.074
3700	34.570	80189	244.336	222.663
3800	35.849	83710	245.275	223.246
3900	37.139	87360	246.223	223.823
4000	38.433	91138	247.180	224.395
4100	39.719	95046	248.144	224.962
4200	40.990	99081	249.117	225.526
4300	42.236	103243	250.096	226.086
4400	43.450	107528	251.081	226.643
4500	44.624	111932	252.071	227.197
4600	45.752	116451	253.064	227.748
4700	46.828	121080	254.059	228.298
4800	47.847	125815	255.056	228.845
4900	48.805	130648	256.053	229.390
5000	49.698	135573	257.048	229.933
5100	50.525	140585	258.040	230.474
5200	51.285	145676	259.029	231.014
5300	51.976	150840	260.012	231.552
5400	52.599	156069	260.990	232.088
5500	53.154	161357	261.960	232.622
5600	53.643	166698	262.922	233.155
5700	54.068	172084	263.876	233.685
5800	54.431	177509	264.819	234.214
5900	54.735	182968	265.752	234.741
6000	54.982	188455	266.674	235.265

VAPOUR PRESSURE DATA

T K	P bar	ΔG° J mol^{-1}	ΔH° J mol^{-1}
298.15	2.06E-129	734544	780000
300	1.43E-128	734262	779992
400	1.26E-94	719087	779529
500	2.83E-74	704037	779002
600	1.02E-60	689097	778423
700	4.87E-51	674257	777802
800	8.70E-44	659510	777142
900	3.76E-38	644848	776446
1000	1.20E-33	630264	775721
1100	5.77E-30	615756	774966
1200	6.70E-27	601315	774186
1300	2.61E-24	586942	773382
1400	4.32E-22	572631	772554
1500	3.60E-20	558381	771705
1600	1.72E-18	544187	770835
1700	5.18E-17	530049	769948
1800	1.07E-15	515963	769044
1900	1.59E-14	501927	768125
2000	1.81E-13	487942	767195
2100	1.62E-12	474003	766255
2200	1.19E-11	460107	765309
2300	7.34E-11	446256	764360
2400	3.87E-10	432446	763410
2500	1.79E-9	418675	762465
2600	7.32E-9	404942	761526
2700	2.70E-8	391246	760598
2800	9.04E-8	377581	759683
2900	2.78E-7	363952	758782
3000	7.94E-7	350352	757899
3100	2.12E-6	336781	757033
3200	5.29E-6	323238	756187
3300	1.25E-5	309720	755357
3400	2.81E-5	296228	754543
3458(s)	4.40E-5	288414	754077
3458(l)	4.40E-5	288414	720002
3500	5.94E-5	283178	719259
3600	1.18E-5	270744	717577
3700	2.25E-4	258352	716019
3800	4.15E-4	246001	714588
3900	7.42E-4	233688	713286
4000	1.28E-3	221404	712112
4100	2.16E-3	209153	711068
4200	3.56E-3	196922	710151
4300	5.70E-3	184712	709361
4400	8.95E-3	172518	708694
4500	1.38E-2	160337	708146
4600	2.08E-2	148172	707714

T K	P bar	ΔG° J mol^{-1}	ΔH° J mol^{-1}
4700	3.08E-2	136006	707391
4800	4.49E-2	123854	707174
4900	6.45E-2	111704	707055
5000	9.12E-2	99555	707028
5100	0.127	87405	707088
5200	0.175	75254	707227
5300	0.239	63096	707439
5400	0.322	50935	707716
5500	0.428	38771	708052
5600	0.565	26598	708442
5700	0.738	14422	708876
5800	0.955	2232	709349
5900	1.225	-9969	709856
6000	1.560	-22170	710391

Re (s,l) = Re (g,bar)

P bar	T K
1E-12	2077
1E-11	2191
1E-10	2318
1E-9	2461
1E-8	2623
1E-7	2809
1E-6	3023
1E-5	3273
1E-4	3575
1E-3	3954
1E-2	4425
1E-1	5027
1	5818
NBP	5824

NBP : normal boiling point at one atmosphere (1.01325 bar)

$\Delta H°_0$ 779.136 ± 6.000 kJ mol^{-1}

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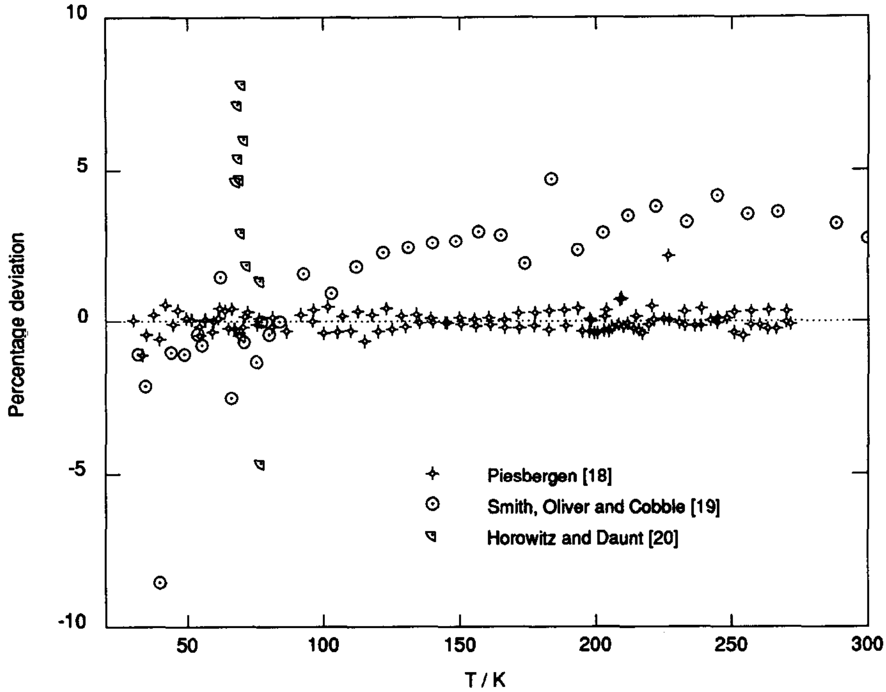

Figure 1: Low Temperature Specific Heat measurements of Rhenium. Percentage deviation from selected values.

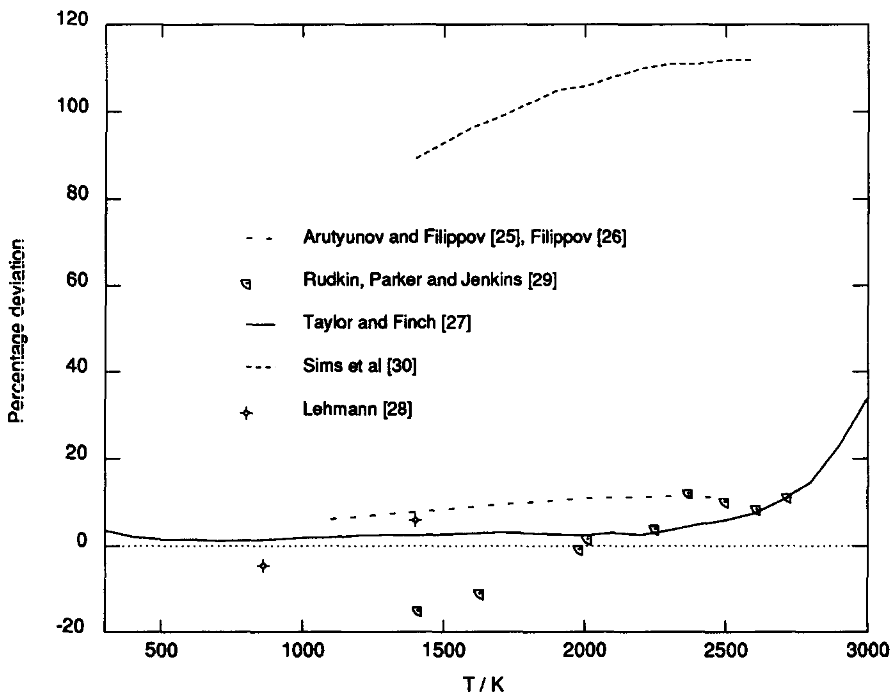

Figure 2: High Temperature Specific Heat measurements of Rhenium. Percentage deviation from selected values.

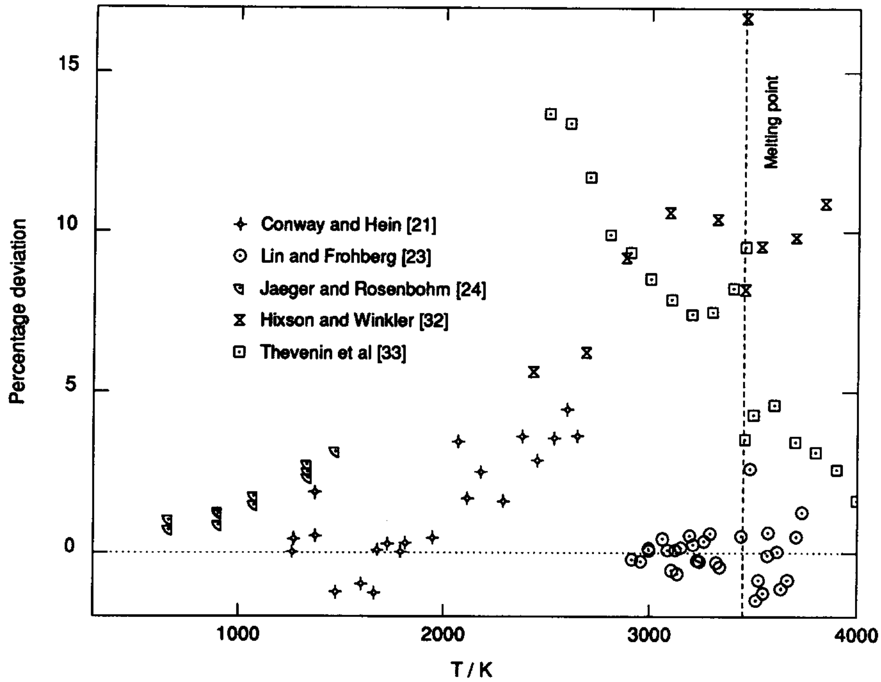

Figure 3: High Temperature Enthalpy measurements of Rhenium. Percentage deviation from selected values.