DOE/MC/30012-~~5856~~-14

ADVANCED SULFUR CONTROL CONCEPTS IN HOT-GAS DESULFURIZATION TECHNOLOGY

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Contract No. DE-AC21-94MC30012-14

Quarterly Report 14

July - October 1997

97 OCT 31 PM 2:50

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October 1997

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EXECUTIVE SUMMARY

Only limited progress was made during the quarter. No CeO_2 sulfidation-regeneration tests were conducted due to continuing problems with the new flame photometric detector (FPD) for the gas chromatograph. The FPD was delivered in late June and was still not working properly by the end of September. Shimadzu personnel made repeated visits during the quarter with each visit seeming to produce marginal improvement in FPD performance. We are now hopeful that the detector will become operable in early October.

Experimental work during the quarter was limited to a series of CeO_2 reduction tests using an atmospheric pressure electrobalance reactor. Both Rhonc-Poulenc and Molycorp CeO_2 were tested over a temperature range of 600 to 1000°C in various reducing gas compositions. Experimental results are in reasonable agreement with equilibrium calculations of the oxygen partial pressure from CHEMQ coupled with earlier experimental results from Bevan and Kordis. Weight loss corresponding to the reduction of CeO_2 to $CeO_{1.86}$ was observed at 1000° in an atmosphere of 40% H_2, 3.5% CO_2, balance He. Helium was used as the carrier gas instead of nitrogen to reduce aerodynamic noise, and the H_2 and CO_2 concentrations were chosen since this mixture results in oxygen partial pressure similar to those expected in Shell gas. The experimental value of $CeO_{1.86}$ compares quite favorably to the predicted value of $CeO_{1.83}$. One unexpected results was a weight loss of about 9% from Rhone-Poulenc CeO_2 in an inert atmosphere at 600°C. This suggests that the as-received material is actually $CeO_2 \bullet H_2O$ instead of anhydrous CeO_2. The theoretical weight loss in converting $CeO_2 \bullet H_2O$ to CeO_2 is 9.45%. In contrast, the Molycorp CeO_2 lost of 0.4% of its original weight in the inert atmosphere at 600°C.

Professor Jothimurugesan of Hampton University was kind enough to provide BET surface area measurements of nine samples consisting of as-received CeO_2 (both Rhone Poulenc and Molycorp), as-received Al_2O_3, both CeO_2 samples with Al_2O_3 as initially charged to the reactor, and both CeO_2-Al_2O_3 mixtures after multicycle sulfidation-regeneration tests. The BET surface area of the Rhone-Poulenc CeO_2 was about 20 times larger than the surface area of Molycorp CeO_2 which explains differences in sulfidation performance reported earlier.

Finally a more complete search of the literature for thermodynamic data for cerium compounds was carried out. It appears that the free energy of formation of CeO_2 as a function of temperature is well defined. Data from four sources are effectively identical. Three data sources were located for the free energy of formation of Ce_2O_3. While there was some disagreement, the difference between the maximum and minimum values is less than 2%. Two sources of data for Ce_2O_2S which contained significant differences were located. Surprisingly, free energy of formation data for the nonstoichiometric oxides $CeO_{1.83}$ and $CeO_{1.72}$ were found in the 1977 data tabulation of Barin et al. We treat these data with suspicion since they were removed from the 1993 tabulation of Barin et al. However, they are reported here for completeness.

FLAME PHOTOMETRIC DETECTOR

The flame photometric detector (FPD) will enable us to measure H_2S concentrations well below the current 100 ppmv limit of the thermal conductivity detector (TCD). The FPD was delivered near the end of the previous quarter and Shimadzu representatives appeared for installation in early July. Pasts were missing from the original shipment which turned out to be the first of many frustrating delays in installation. After repeated visits by Shimadzu personnel the detector was still not operating as expected at the end of the present quarter. When missing parts were finally received and installation was complete, the detector lacked the necessary sensitivity. This is illustrated in Figures 1 and 2 which show FPD chromatograms resulting from the analysis of samples containing108 ppmv H_2S in N_2 and 20 ppmv H_2S in N_2, respectively. The small signal-to-noise ratio illustrated in Figure 2 makes it impossible to achieve reproducible quantitative results at this concentration. In fact, when a sample containing 10 ppmv was analyzed, the signal-to-noise ratio was too small to provide definite peak identification.

Several subsequent visits by Shimadzu each produced marginal sensitivity improvement. The status at the end of the quarter is illustrated in Figure 3 and 4, which show FPD chromatograms for 20 ppmv H_2S in N_2 and 5 ppmv H_2S in N_2, respectively. Improvement can be seen by comparing Figures 2 and 3. Note first that the voltage scale (y-axis) had to be expanded in Figure 3 to show the entire peak. The peak area increased by a factor 92 (from an area of 6594 in Figure 2 to 607,002 in Figure 3) and the signal-to-noise ratio improved proportionally. The peak in Figure 4 corresponding to 5 ppmv H_2S is clearly visible and the signal-to-noise ratio is acceptable. Thus, by the end of the quarter the sensitivity is such as to permit analysis at the sub-five ppmv level.

The remaining problem concerns peak tailing. The long tail, which is obvious in both Figures 3 and 4, means that it is impossible to set the computer integration parameters so that the peak areas are reproducible. At the end of the quarter Shimadzu representatives were attributing the tail to adsorption/desorption of H_2S on stainless steel surfaces. The solution is to replace all possible stainless steel surfaces with teflon or fused silica. This should be accomplished in early October.

BET SURFACE AREA

Dr. K. Jothimurugesan of Hampton University generously agreed to perform BET surface area measurements on various sorbents sample. A description of the nine samples tested and the resultant BET surface areas is presented in Table 1. Figure 5 is a diagram showing the variation of surface area as a result of processing and reaction.

The surface areas of the as-received Rhone-Poulenc CeO_2 having a particle diameter of less than 75 microns and the Al_2O_3 having a particle diameter range of 80 to 200 microns were both approximately 200 m^2/g. Excessive pressure drop across the fixed bed caused by the small particle size led us to process CeO_2 by dry pressing tablets followed by crushing and sieving, with the 150-300 microns particle size range mixed with Al_2O_3 used in the reactor. This process reduced the pressure drop to an acceptable level and also caused an almost 30% reduction in surface area to 156 m^2/g. The same processing steps were used with the Molycorp CeO_2 with the surface actually

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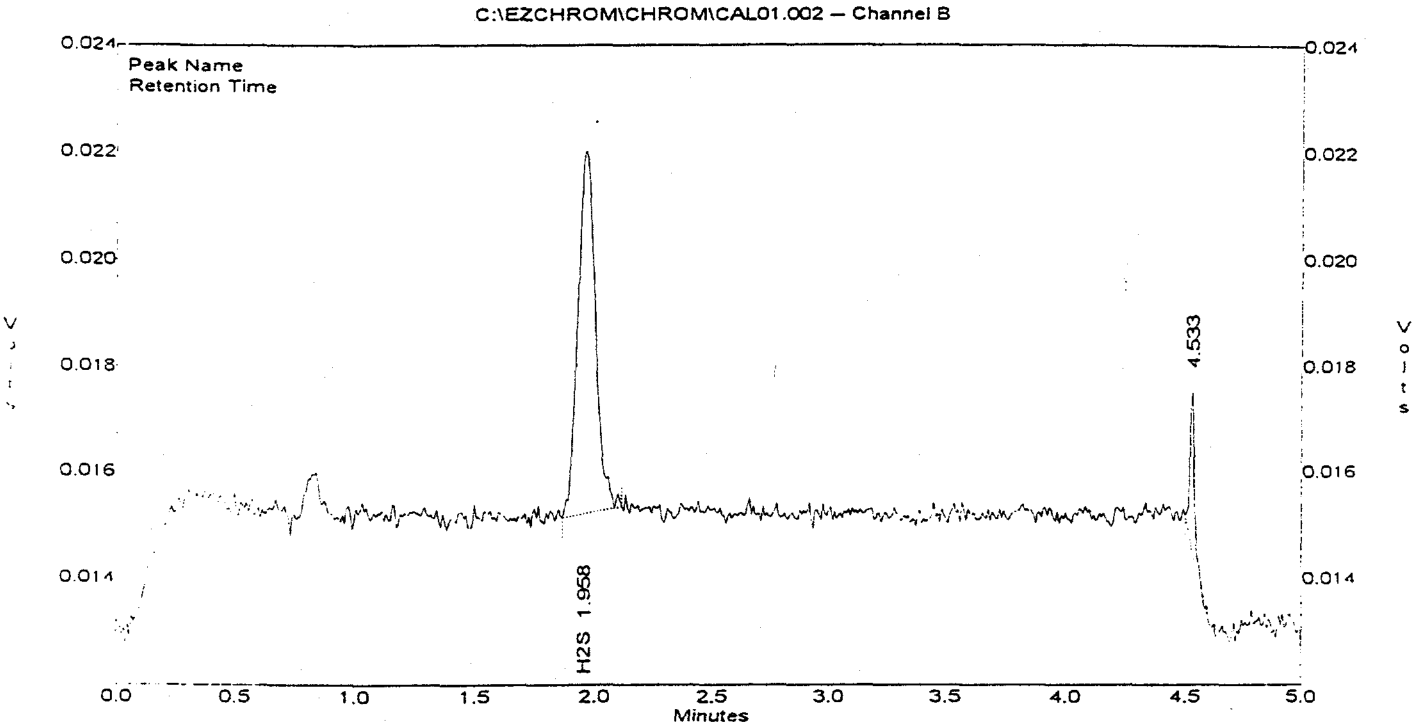

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Channel B Results

Peak  Name                  Time    Area        Area %   ESTD Conc   NORM Conc
----  -----------------    ------  ---------   -------  ---------   ---------
  1   H2S                    1.96      34931    89.098      0.020     100.000
 --   SO2                    3.51          0     0.000      0.000       0.000

Totals :

                                       34931    89.098      0.020     100.000
```

Figure 1. FPD Chromatogram for 108 ppmv H_2S in N_2 (Initial Results)

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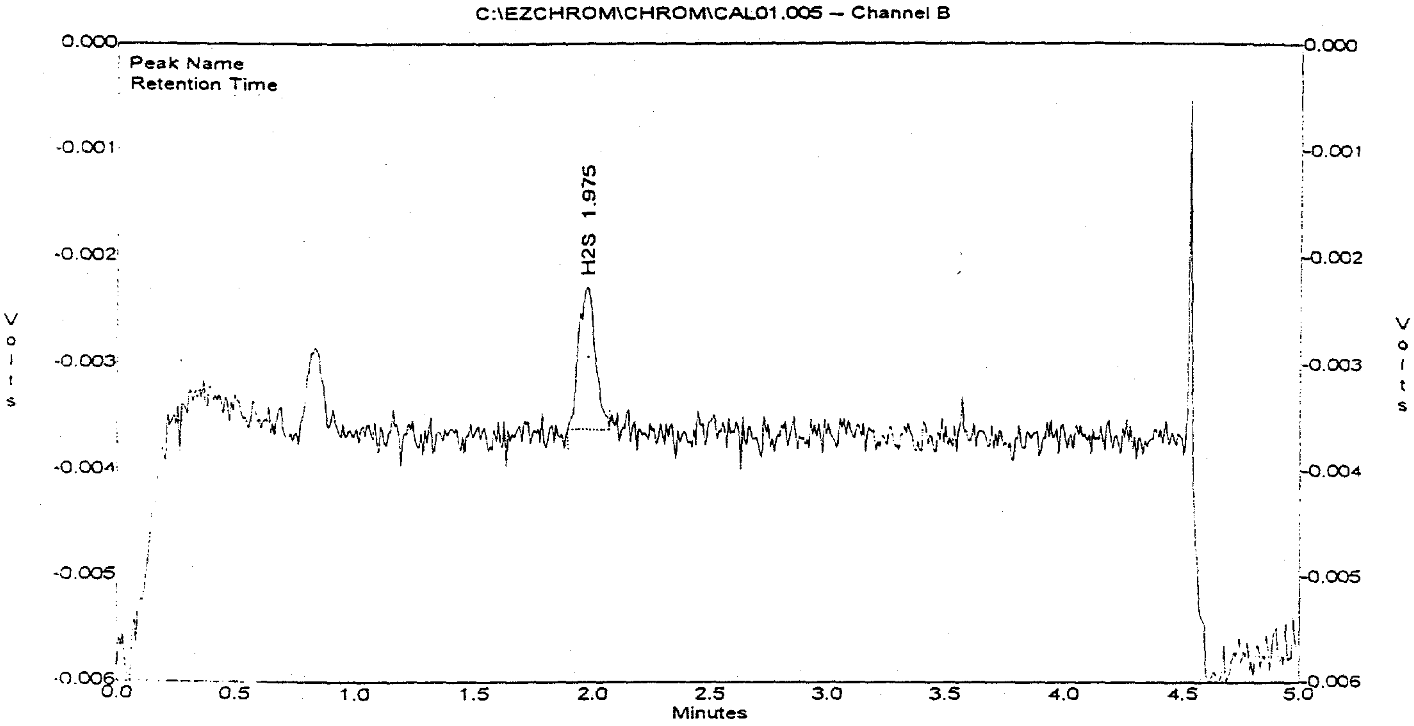

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Channel B Results

Peak  Name                 Time     Area        Area %    ESTD Conc    NORM Conc
----  -----------------   ------  ---------    -------   ---------    ---------
  1   H2S                   1.98       6594    100.000       0.002      100.000
      SO2                   3.51          0      0.000       0.000        0.000

Totals :
                                       6594    100.000       0.002      100.000
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Figure 2. FPD Chromatogram for 20 ppmv H_2S in N_2 (Initial Results)

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                                                                Page 1 of 1

 File          : C:\EZCHROM\CHROM\TEST2.007
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 Sample ID     :

                        Sample Amount       ISTD Amount         Mult. Factor
 Calibration :             1.000               1.000               1.000
 Run         :             1.000               1.000               1.000

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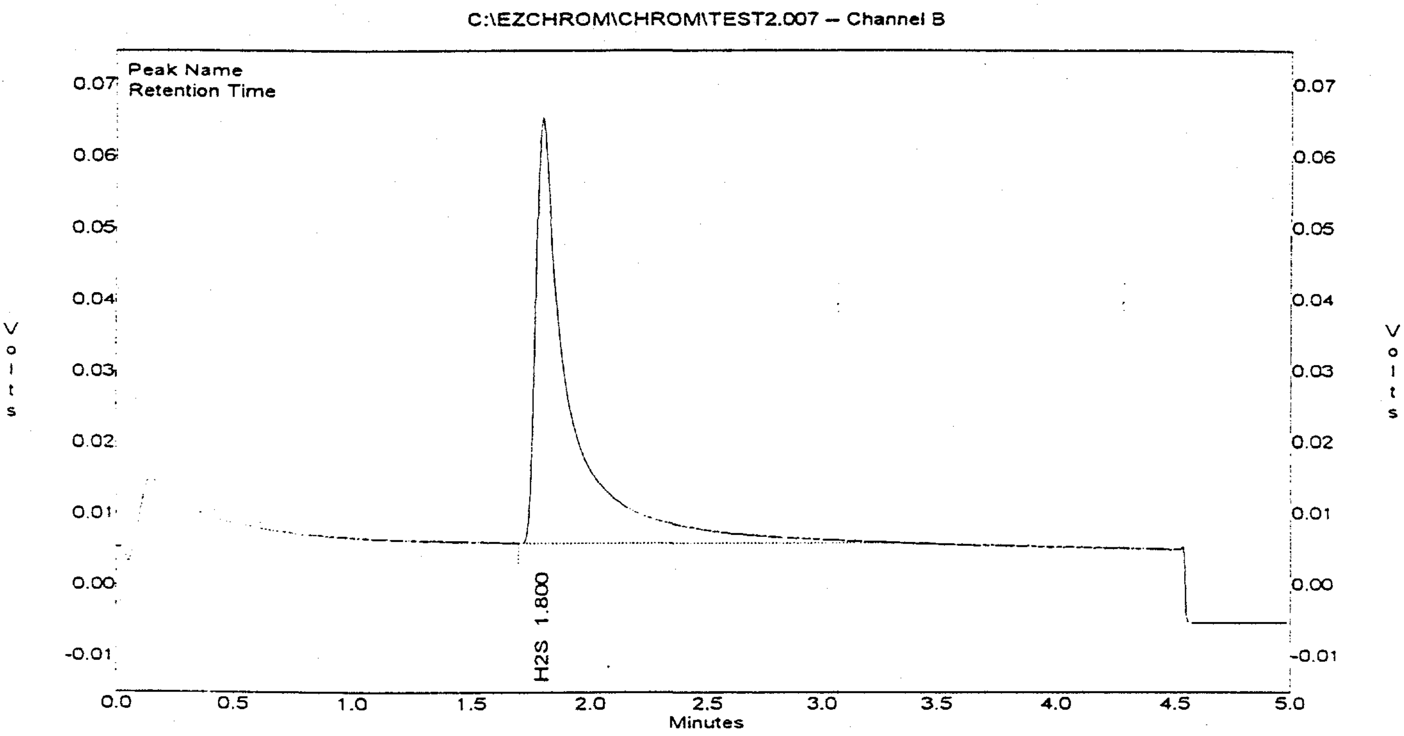

```
Channel B Results

 Peak  Name                  Time     Area        Area %   ESTD Conc    NORM Conc
 ----  -----------------   ------  ---------    -------  ---------    ---------
    1  H2S                   1.80     607002    100.000      0.000        0.000

Totals :
                                      607002    100.000      0.000        0.000
```

Figure 3. FPD Chromatogram for 20 ppmv H_2S in N_2 (Current Results)

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                                                                    Page 1 of 1

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Sample ID      :

                     Sample Amount       ISTD Amount         Mult. Factor
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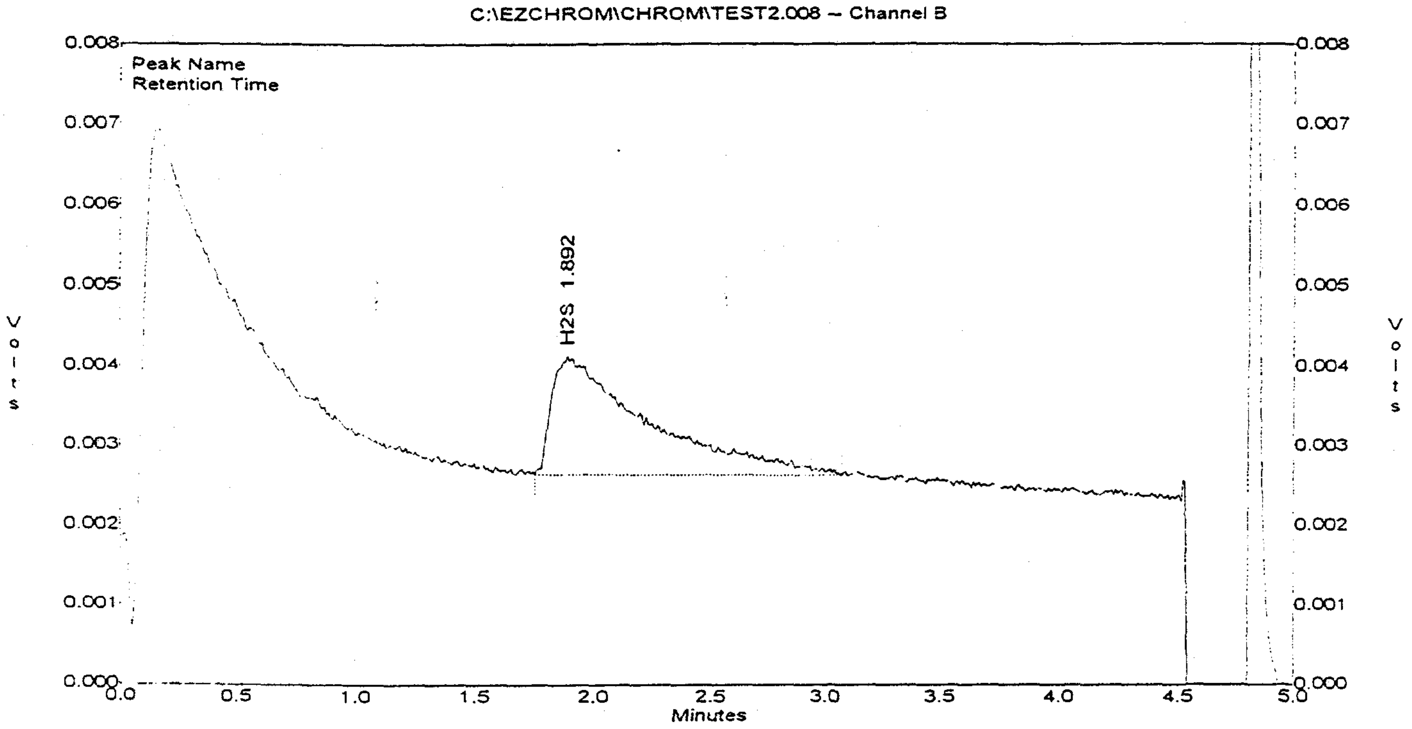

```
Channel B Results

Peak  Name                   Time     Area        Area %    ESTD Conc   NORM Conc
----  -----------------     ------   ---------   -------   ---------   ---------
   1  H2S                     1.89       41444   100.000       0.000       0.000

Totals :
                                         41444   100.000       0.000       0.000
```

Figure 4. FPD Chromatogram for 5 ppmv H_2S in N_2 (Current Results)

Table 1. BET Surface Areas of Sorbent Samples

		Surface Area, m^2/g
1.	CeO_2 from Rhone-Poulenc (as-received)	220
2.	CeO_2 from Molycorp (as-received)	9.6
3.	Al_2O_3 (inert diluent) (as-received)	217
4.	CeO_2 from Rhone-Poulenc (after tabletting, crushing and sieving)	156
5.	CeO_2 from Molycorp (after tabletting, crushing and sieving)	11.2
6.	CeO_2-Al_2O_3 Reactor Charge (Rhone-Poulenc CeO_2: 2 CeO_2: 1 Al_2O_3 by mass)	181
7.	CeO_2-Al_2O_3 Reactor Charge (Molycorp CeO_2: 2 CeO_2 : 1 Al_2O_3 by mass)	74
8.	Run Ce-16 Sorbent (Rhone-Poulenc CeO_2: Al_2O_3 mixture after 10-cycle run Ce-16)	23
9.	Run Ce-23 Sorbent (Molycorp CeO_2, Al_2O_3 mixture after 4-cycle run Ce-23)	15

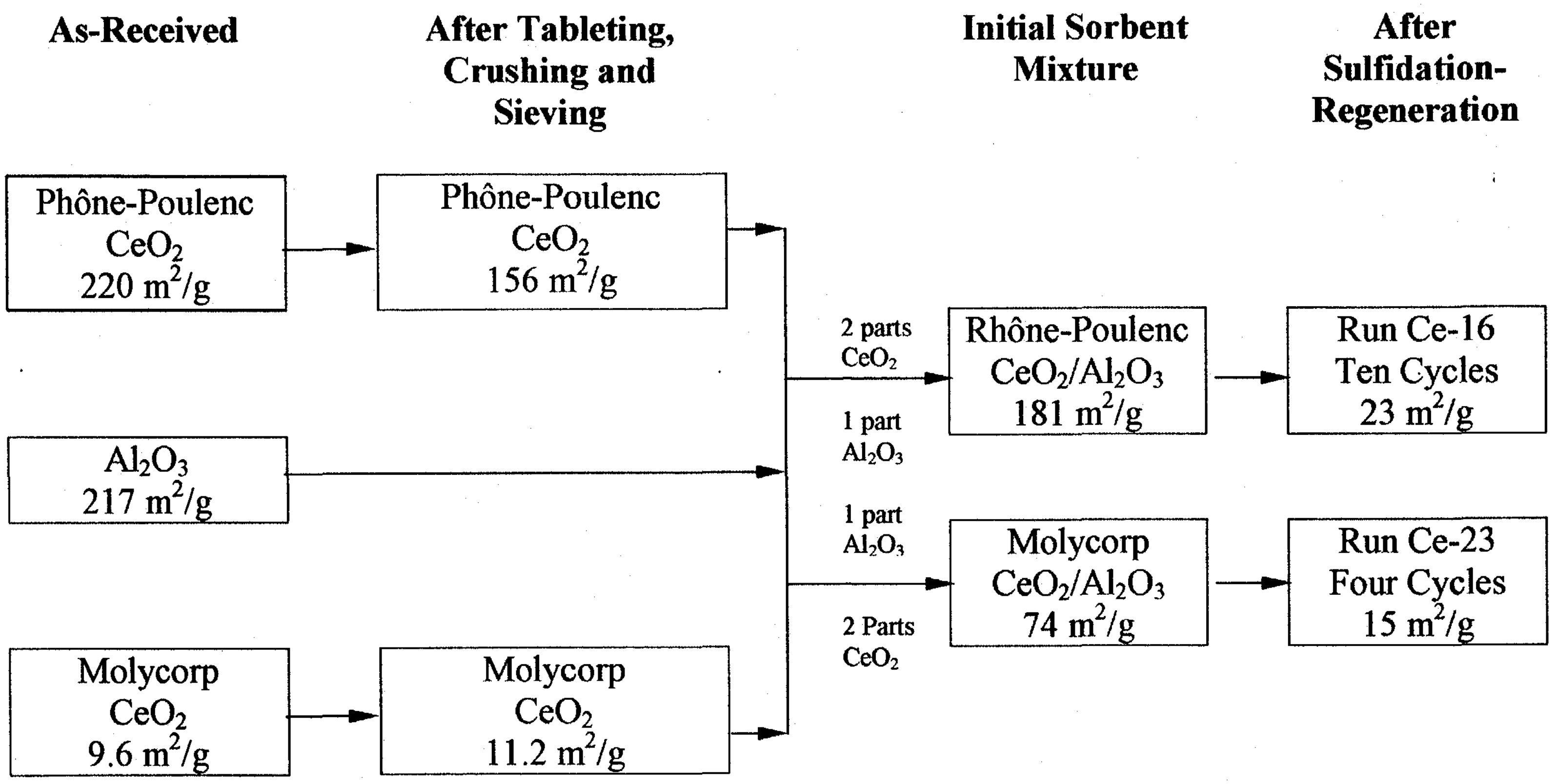

Figure 5. Sorbent Surface Area Variations at Various Processing Stages

showing a small increase from 9.6 to 11.2 m^2/g during the tableting, crushing, and sieving process. The significantly larger surface area of the Rhone-Poulenc sample is consistent with experimental sulfidation results. The duration of the prebreakthrough period was about 100 minutes using Rhone-Poulenc CeO_2 and only about 30 minutes using Molycorp CeO_2.

The reactor charge consisted of 1 part by mass of Al_2O_3 and 2 parts CeO_3 from either Rhone-Poulenc or Molycorp. The measured surface areas of the mixtures were in agreement with calculated surface areas based on the combination of the components. The sorbents following ten-cycle run Ce-16 using Rhone-Poulenc CeO_2 and four-cycle run Ce-23 using Molycorp CeO_2 lost surface area to values of 23 m^2/g and 15 m^2/g, respectively. There is likely greater error involved in these measurements since the sorbent removed from the reactor after reaction was mixed with quartz wool. The quartz wool was separated to the extent possible but it is likely that low surface area quartz wool remaining with the sorbent contributed to the low measured surface area. In spite of the surface area lost during reaction, it is encouraging that sulfidation and regeneration tests were quite reproducible throughout the multicycle tests.

CERIUM OXIDE REDUCTION

The possibility of achieving prebreakthrough concentrations approaching the 20 ppmv target levels appears to depend on the extent of reduction of CeO_2 to nonstoichiometric CeO_n when exposed to a highly reducing gas such as that from a Shell gasifier. Various aspects of estimating the equilibrium value of n as a function of gas composition and temperature were discussed in the previous quarterly report.

During the present quarter a limited number of experimental reduction tests were conducted to compare results with theory. An atmospheric electrobalance reactor was used to monitor solid mass as a function of temperature and gas composition. The temperature range covered was 600 to 1000 °C and the feed gas contained 3.5% CO_2 and 40% H_2 in helium. Helium was used as the inert gas instead of nitrogen as it produced less aerodynamic noise and permitted increased electrobalance sensitivity. The CO_2 and H_2 concentrations were chosen to provide an approximate match to the equilibrium O_2 pressure of Shell gas over the temperature range of interest. The equilibrium O_2 pressures as calculated from CHEMQ are compared in Table 2.

The test procedure was as follows. Processed sorbents were heated to 600 °C in helium and held at that temperature until the weight was constant. H_2 and CO_2 were then introduced. The temperature was increased in 50 °C or 100 °C increments to 1000 °C and held isothermally at each increment until the weight was constant. Interestingly, the Rhonc-Poulenc CeO_2 lost 9% of its original weight (from 8.73% to 9.23% in three separate tests) at the end of the 600 °C treatment in inert gas. This suggest that the Rhone-Poulenc material is actually $CeO_2{\bullet}H_2O$ as complete decomposition of pure monohydrate would produce a theoretical weight loss of 9.45%. This is also consistent with material balance results from previous sulfidation-regeneration tests. For example, in the earlier ten-cycle run Ce-16, the average amount sulfur removed during sulfidation and liberated during regeneration were 87.2% and 91.8%, respectively, of stoichiometric. These stoichiometric values were based on the assumption of pure CeO_2. Correcting for the weight loss,

Table 2. Comparison of Equilibrium Oxygen Pressure From Shell Gas and Experimental Gas as a Function of Temperature, P = 1 atm.

T, °C	Equilibrium O_2 Pressure, atm	
	Shell Gas[1]	Experimental Gas[2]
600	6.79×10^{-25}	3.02×10^{-26}
650	1.00×10^{-23}	6.76×10^{-25}
700	9.33×10^{-23}	1.30×10^{-23}
750	5.74×10^{-22}	2.28×10^{-22}
800[3]	2.84×10^{-21}	3.39×10^{-21}
850	2.80×10^{-20}	4.09×10^{-20}
900	4.28×10^{-19}	4.02×10^{-19}
950	4.01×10^{-18}	3.30×10^{-18}
1000	3.15×10^{-17}	2.29×10^{-17}

Nominal Composition

[1]Shell Gas	[2]Experimental Gas
60% CO	40% H_2
29% H	56.5% He
2% CO_2	3.5% CO_2
5% H_2O	
1% H_2S	

[3]Carbon deposition is favored in the Shell gas at T ≤800°C.

the sulfidation average increases to 95.8% of stoichiometric and the regeneration average to 100.9% stoichiometric. In contrast, the weight loss during exposure of Molycorp CeO_2 in helium at 600°C was only 0.4%, which we attribute to the desorption of physically adsorbed moisture.

The equilibrium value of n in CeO_n as a function of temperature is shown in Figures 6 and 7 for Molycorp and Rhone-Poulenc CeO_2, respectively. The values are based on the assumption that both samples were pure CeO_2 following treatment at 600°C in helium. The dashed line in both figures is based on predicted P_{O_2} for a Shell gas using CHEMQ coupled with the results of Bevan and Kordis (1955), which serve as "theoretical" values. Two experimental runs were carried out using each sorbent and the results are quite reproducible.

The trends in the experimental results from both samples are in general agreement with theory. The largest differences were at 800°C where the experimental values were 1.95 for Molycorp CeO_2 (Figure 6) and 1.97 for Rhone-Poulenc CeO_2 (Figure 7) compared to the theoretical value of 1.97, and at 1000°C where both samples produced experimental values of 1.86 compared to the theoretical value of 1.83.

THERMODYNAMICS DATA

In the lull awaiting installation of the FPD, a more complete literature search for thermodynamic data for cerium compounds was carried out. Surprisingly, free energy of formation data for the nonstoichiometric oxides $CeO_{1.83}$ and $CeO_{1.72}$ were found in the earlier tabulation of Barin et al. (1977). These data must be treated with suspicion since they were removed from the later tabulation (Barin et al., 1993); however, the data are reported here for completeness.

Figure 8 shows free energy of formation data for CeO_2 from four data sources. ΔG_f is a linear function of temperature, and, as shown in the figure, the data are effectively identical. Similar data for $CeO_{1.83}$ from Barin et al. (1977) are shown in Figure 9 along with a single data point at 1000°C from Sorensen (1976). The data from Barin et al. (1973) are also linear with temperature, but the difference between the two values at 1000°C is about 63 kJ/mol, or 7%. A similar plot for $CeO_{1.72}$ showing data from Barin et al. (1977) and a single point from Sorensen (1976) is shown in Figure 10. Again the difference at 1000°C is about 63 kJ/mol. The dashed lines in both Figure 8 and 9 through the points by Sorensen are drawn parallel to the Barin data.

Three complete free energy data sources for Ce_2O_3 ($CeO_{1.5}$) were found as shown in Figure 11. All are effectively linear but there is considerable difference between the data sets. For example, at 1100K the smallest value of -753 kJ/mol is from Barin et al. (1977) while the largest value of -739 kJ/mol is from Gschneidner et al. (1973). The later tabulation by Barin et al. (1993) is at the intermediate value of -743 kJ/mol. The solid line in Figure 11 represents the numerical average of the three data sets.

Finally, free energy data for Ce_2O_2S from Gschneidner et al. (1973) and from Fruehan (1979) plus a single data point at 1073K from Dwivedi and Kay (1984) are shown in Figure 12. The Gschneidner et al. (1973) data were claimed to be accurate within ±63 kJ/mol while the Fruehan

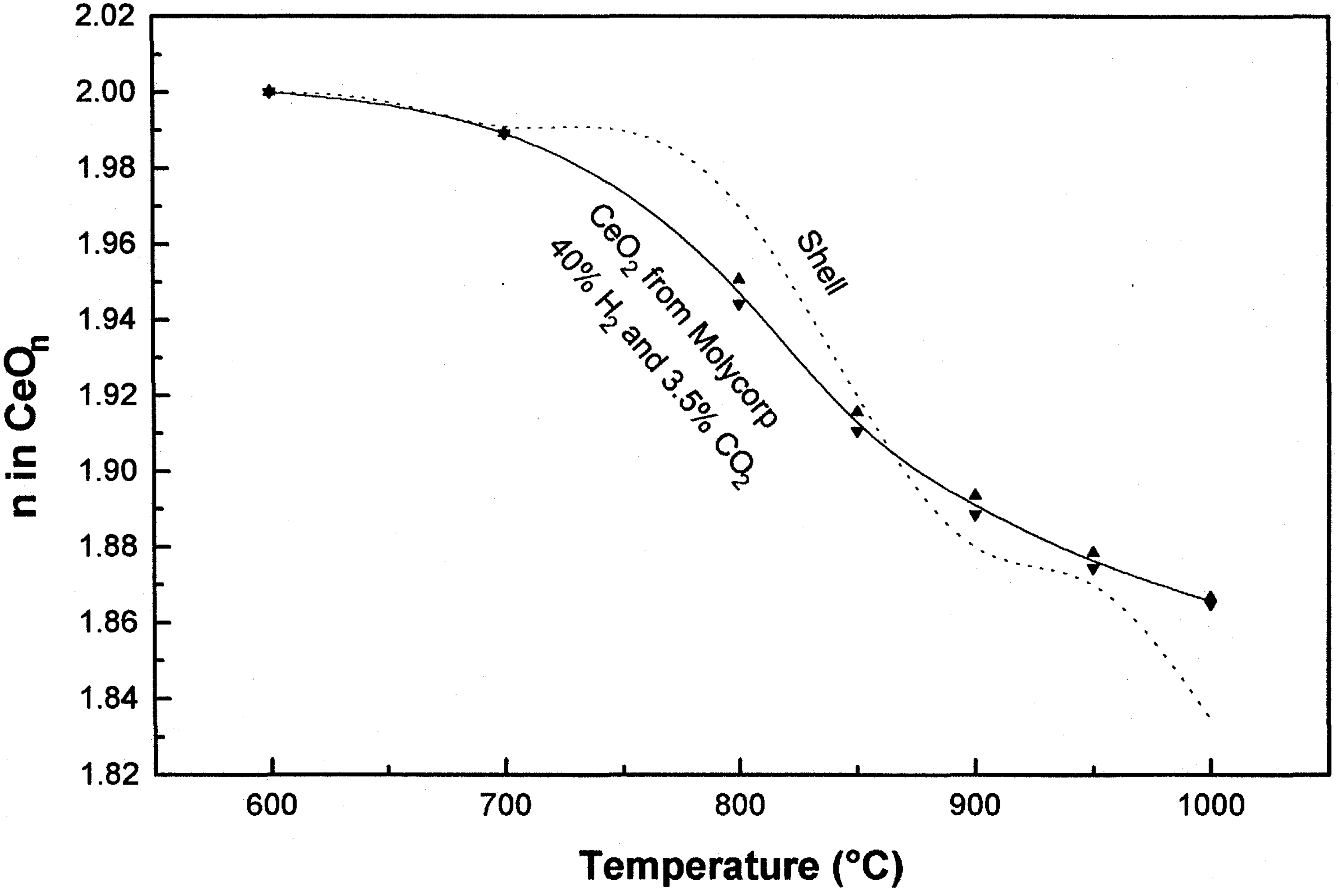

Figure 6. Reduction of Molycorp CeO_2

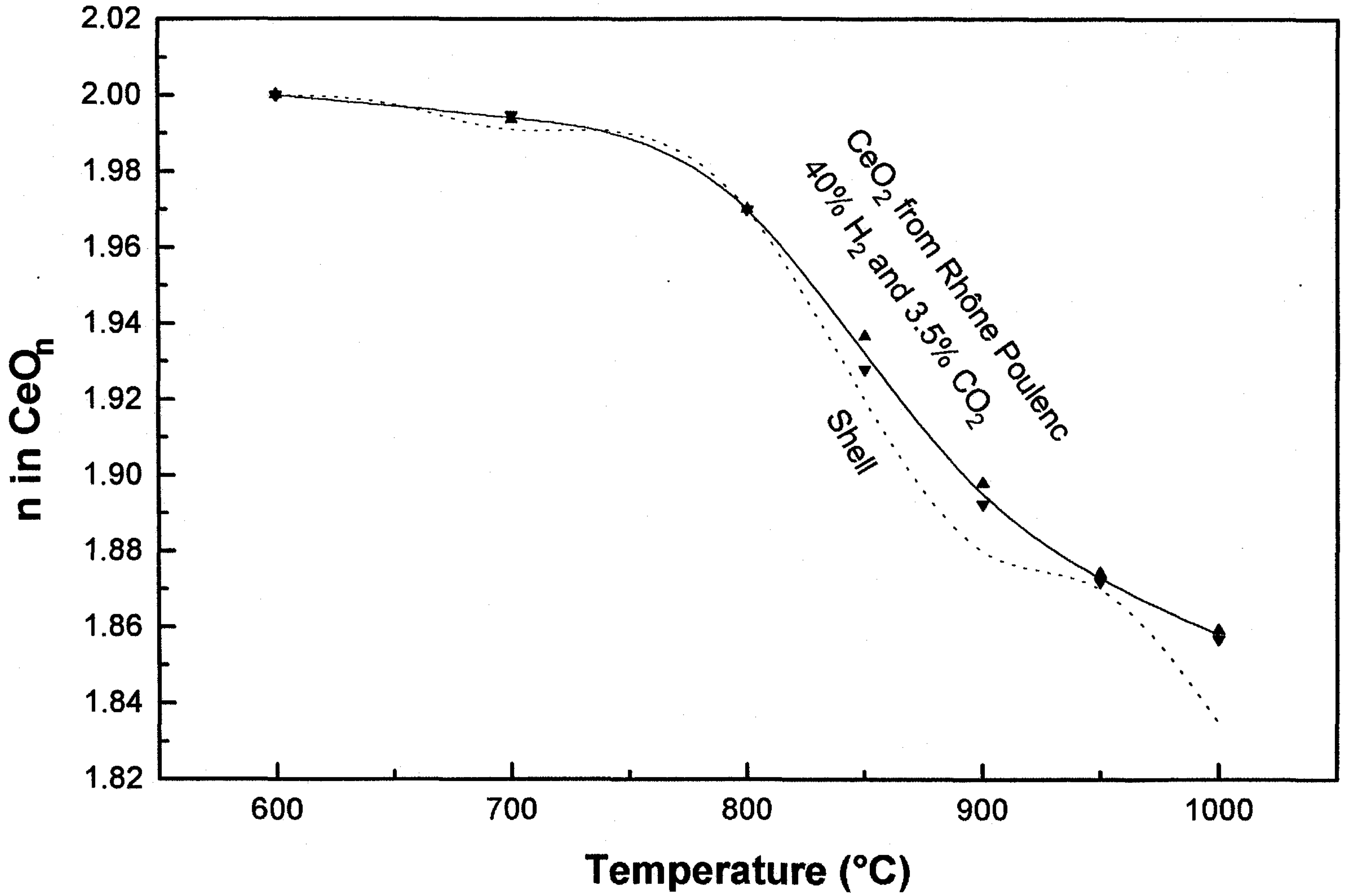

Figure 7. Reduction of Rhone-Poulenc CeO_2

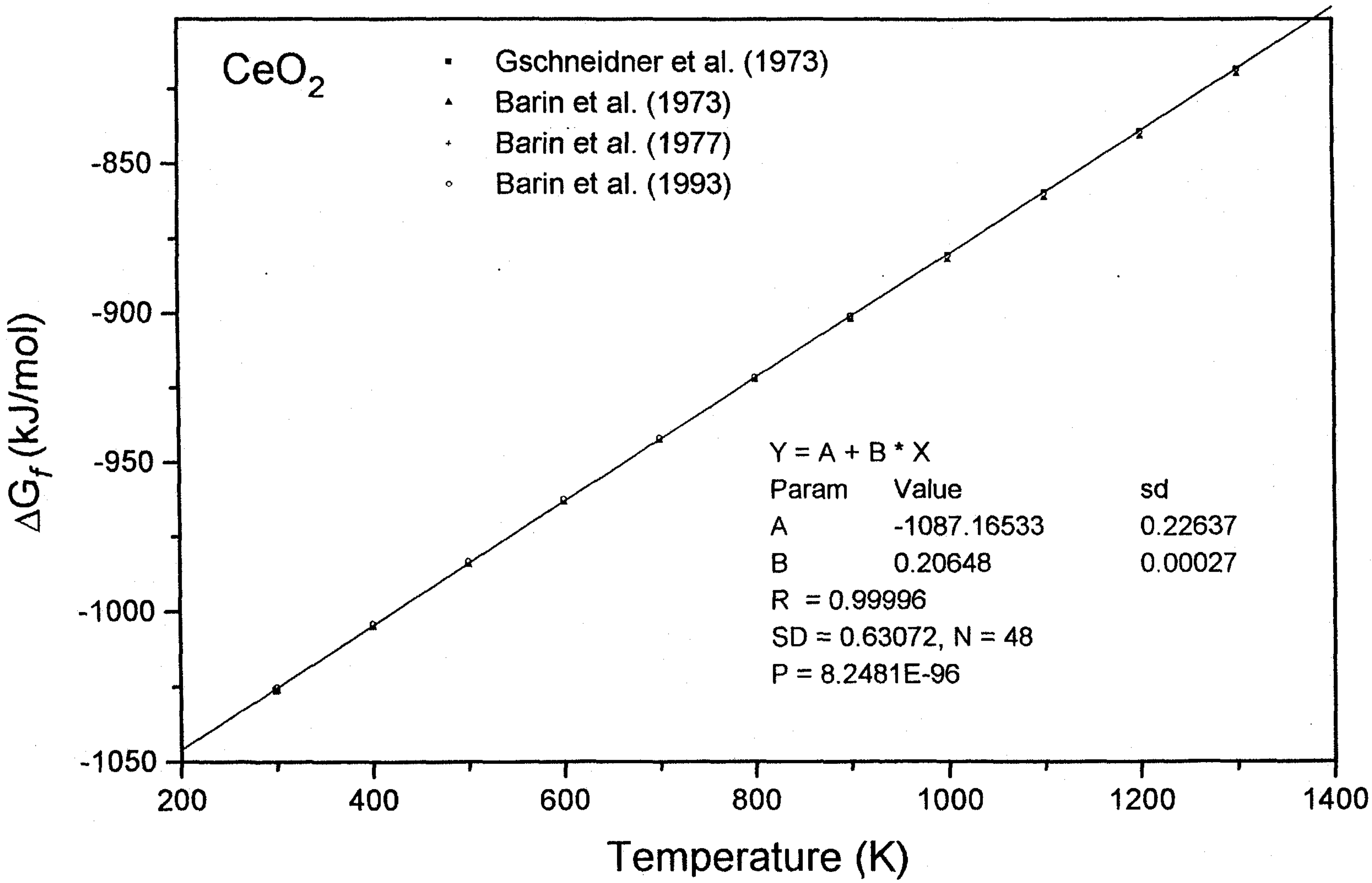

Figure 8. Free Energy of Formation of CeO$_2$ from Four Reference

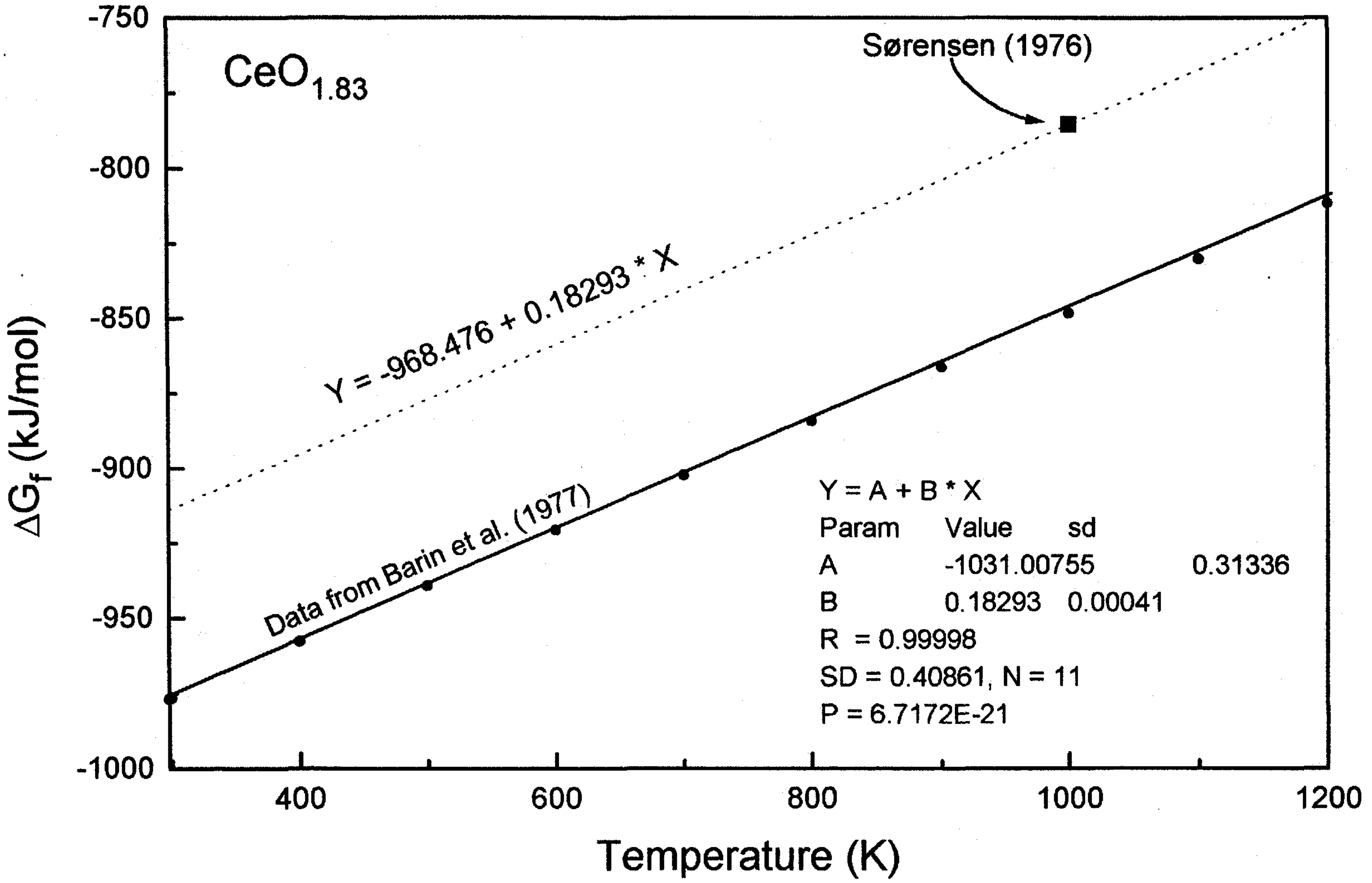

Figure 9. Free Energy of Formation CeO$_{1.83}$

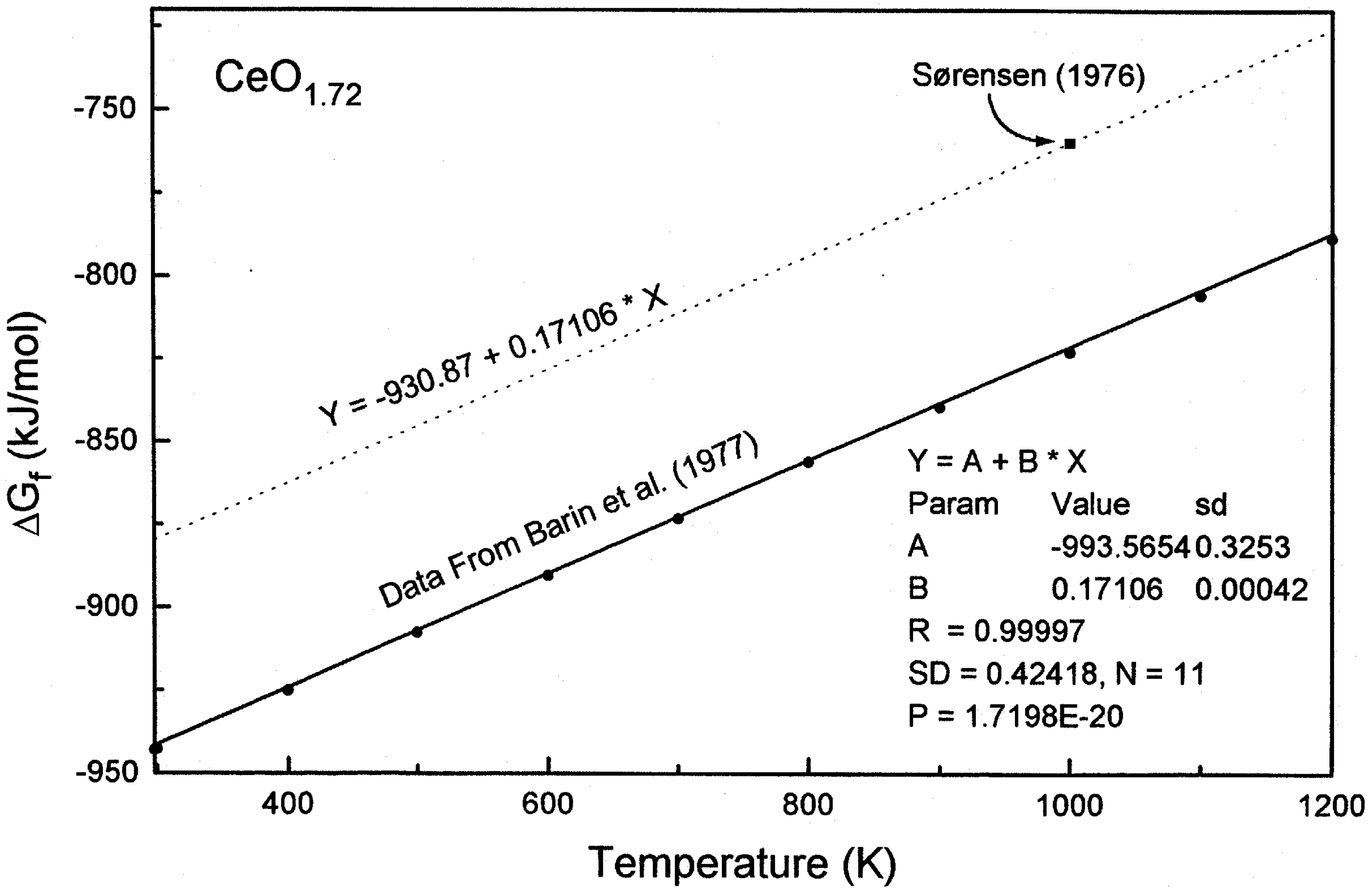

Figure 10. Free Energy of Formation of CeO$_{1.72}$

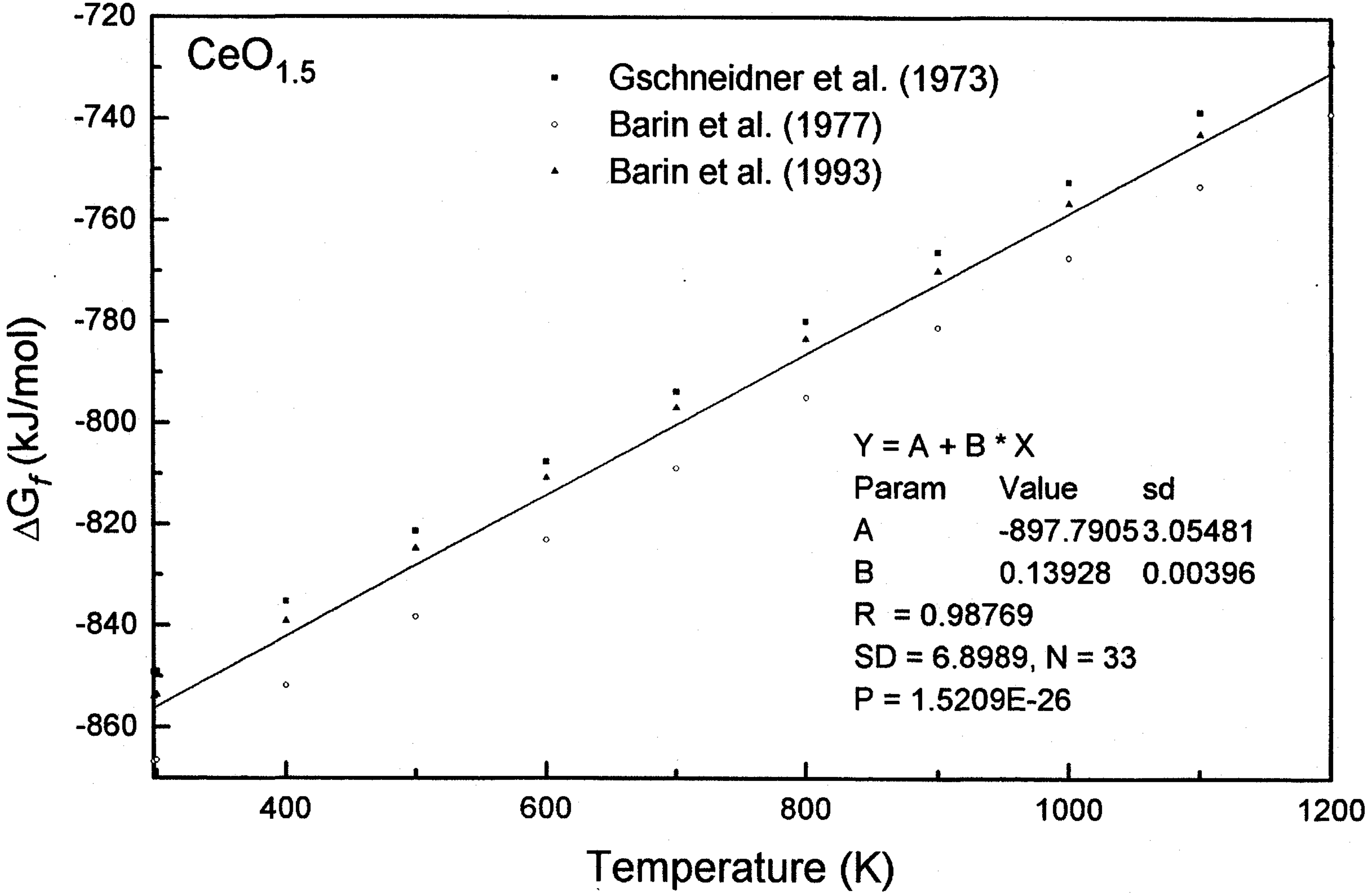

Figure 11. Free Energy Formation of Ce_2O_3 ($CeO_{1.5}$)

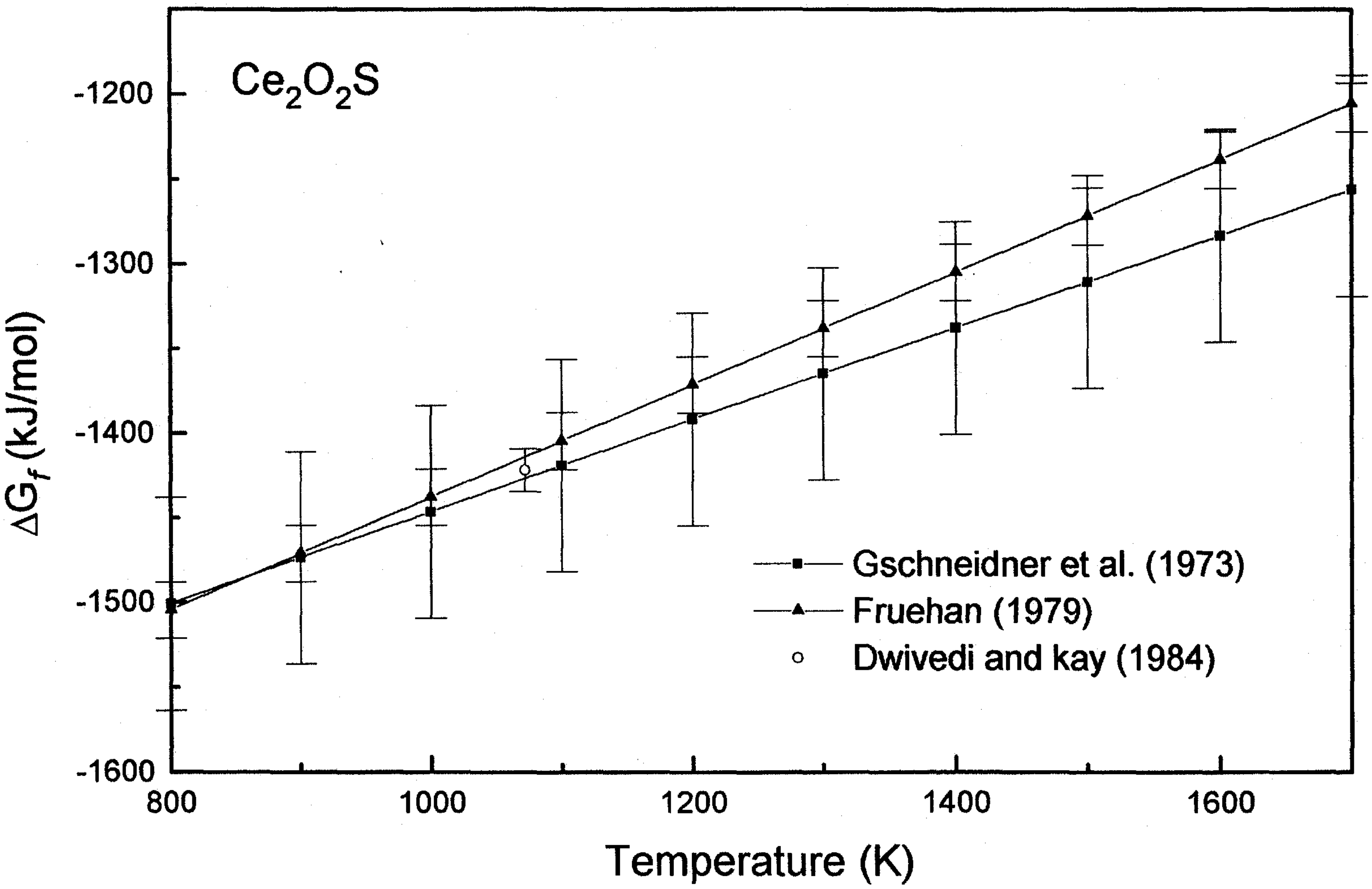

Figure 12. Free Energy Formation of Ce_2

(1979) data were claimed to be accurate within ±15 kJ/mol. Error bars corresponding to these values are shown on the figure. Both data sets are linear with temperature and values from the two sources are reasonably close at low temperature but there is increasing deviation at higher temperature. The single point from Dwivedi and Kay (1984) lies between the two data sets. Values of ΔG_f from Fruehan (1979) are smaller, but all of his data lie within the error bars reported by Gschneidner et al. (1973). In contrast, all of the Gschneidner et al. (1973) data for temperatures equal to or greater than 1200K lie outside the Fruchan error bars.

The free energy values for CeO_2 and Ce_2O_3 in the CHEMQ data base are effectively equal to the values reported by Barin et al. (1993) while the Ce_2O_2S data are similar, but not equal, to the data from Gschneider et al. (1973).

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