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Gibbs Free Energy of Formation of Zircon from Measurement of Solubility in H_2O

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We exploited the large difference in the solubility of SiO_2 and ZrO_2 in H_2O to constrain precisely the Gibbs energy of formation of zircon ($ZrSiO_4$). Solubility in H_2O was determined at 800°C, 1.2 GPa, by weight loss of synthetic zircon crystals. The experiments yielded fine-grained monoclinic ZrO_2 as an incongruent solution product uniformly coating zircon crystals. Experiments on the ZrO_2-coated zircon crystals were also carried out with an initially slightly SiO_2-oversaturated fluid, causing weight gain by zircon regrowth. The mean SiO_2 concentration for forward and reverse experiments was 0.069 ± 0.010 mol/kg H_2O (2σ). When combined with precise activity–composition measurements for aqueous SiO_2, the data constrain the Gibbs free energy of zircon from its oxides at 298 K, 10^5 Pa, to be -19.30 ± 1.16 kJ/mol (2σ). This determination is comparable in precision to the best measurements obtainable by more conventional methods, which suggests that determination of the thermochemical properties of other important ceramic materials may also be amenable to this method.

I. Introduction

Because of its durability, stability, and resistance to thermal shock, zircon is potentially useful in a wide variety of applications. However, its refractory character hinders precise determination of its Gibbs energy of formation,[1,2] ΔG_f°, which is required for computation of phase equilibria involving $ZrSiO_4$. The ΔG_f° of zircon from the oxides

$$\underset{\text{baddeleyite}}{ZrO_2} + \underset{\text{quartz}}{SiO_2} = \underset{\text{zircon}}{ZrSiO_4} \quad (1)$$

has been derived from phase-equilibrium studies[3–5] and high-temperature oxide-melt solution calorimetry,[6] and it is listed in compilations of thermodynamic data;[7–9] however, values differ by over 11 kJ/mol (Table I).

Rosén and Muan[3] made use of the equilibria

$$Co_2SiO_4 + ZrO_2 + 2CO = ZrSiO_4 + 2Co + 2CO_2 \quad (2)$$

and

$$Co_2SiO_4 + 2CO = SiO_2 + 2Co + 2CO_2 \quad (3)$$

The ΔG_f° of zircon was derived from the CO/CO_2 ratios of gases equilibrated with the solid reactants and products of the two reactions at high temperatures. Variation of ΔG_f° with temperature is inconsistent with high-temperature heat capacity data, suggesting a systematic error, perhaps because of Co substitution in zircon.[6] Nevertheless, a value of ΔG_f° of zircon at 298 K, 10^5 Pa, can be derived by combining the derived midpoint ΔG_T° with refitted C_p functions[6] (Table I). The apparently small uncertainty (1.16 kJ/mol, all uncertainties are 2σ unless otherwise noted) is an artifact of the narrow temperature interval over which the measurements were made (1180°–1366°C).

Schuiling *et al.*[4] used hydrothermal synthesis experiments at 1000 K, 0.1 GPa to determine the directions of several possible reactions of zircon with other minerals having reasonably well-defined thermodynamic properties. The equilibria investigated are metastable, but constraints on the Gibbs energy change of reaction 1 were obtained by determining whether the postulated reactions would or would not take place. Only broad limits on Gibbs energy change were derived, leading to a large uncertainty in ΔG_f° of zircon (4.5 kJ/mol).

Determination of the position at high temperature (T) and pressure (P) of the univariant equilibrium

$$\underset{\text{zircon}}{ZrSiO_4} + 2\underset{\text{magnesite}}{MgCO_3} = \underset{\text{forsterite}}{Mg_2SiO_4} + \underset{\text{baddeleyite}}{ZrO_2} + CO_2 \quad (4)$$

also permits derivation of ΔG_f° of zircon. Although dependent on CO_2 equation of state and other data for the minerals, the results indicate ΔG_f° of zircon at 298 K, 10^5 Pa, of -18.44 ± 1.71 kJ/mol.[5,9]

Heat of solution measurements[6] in molten $Pb_2B_2O_5$ yielded a mean enthalpy of reaction 1 at 977 K of -27.90 kJ/mol. This result and refitted heat capacity data[10–12] gave a value of ΔG_f° at 298 K, 10^5 Pa, of -23.57 ± 3.62 kJ/mol (Table I), where the uncertainty is the 95% confidence interval.

The phase-equilibrium and calorimetric results suggest that the Gibbs energy change of reaction 1 is between -18 and -24 kJ/mol at 298 K, 10^5 Pa, neglecting uncertainties in individual constraints. This range only partly overlaps that given in compilations of thermodynamic data in current use for ceramic and geochemical applications[7–9] (Table I), which rely on at least one of the above studies for free energy of formation values or imprecise estimates of the equilibrium temperature of reaction 1 at 10^5 Pa.[13] Sources of uncertainty in Gibbs energy of formation include experimental errors, the finite width of bracketing

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Table I. Summary of ΔG_f° of Zircon From the Oxides at 298 K, 10^5 Pa

ΔG_f° (kJ/mol)	2σ (kJ/mol)	Methods	Source
Experiment			
−20.79	1.16	High-T redox equilibria, 10^5 Pa, 1515–1639 K	3
−24.28	4.50	Monotropic reactions, 100 MPa, 1000 K	4
−23.57	3.62	High-T solution calorimetry, 10^5 Pa, 977 K	6
−18.44	1.71	High-PT phase equilibrium (0.7–1.1 GPa, 1073–1173 K)	5
−19.30	1.16	High-PT solubility, 1.2 GPa, 1073 K	This work
Compilations			
−13.20	—		7
−19.81	3.10		8
−17.32	3.44		9

All ΔG_f° values corrected to 298 K, 10^5 Pa, using thermal functions[6] and expansivity and compressibility.[9] Uncertainties reflect errors in experimental results, and ignore those in ZrO_2 and SiO_2 thermochemical data. Uncertainty for the value from Ellison and Navrotsky[6] is the 95% confidence interval. Value from Ferry *et al.*[5] calculated using data from Holland and Powell.[9] Dash denotes no uncertainties given.

constraints derived from phase-equilibrium studies, and any errors in other thermochemical data used. The values in Table I omit the latter source because they were calculated using the same expansivity, compressibility, and thermal functions.[6,9] Thus, improving the precision of phase-equilibrium determination of ΔG_f° of zircon is required to reduce the wide scatter in Table I.

Precise measurement of aqueous silica solubility at elevated T and P, by gravimetry of quenched phases or by chemical analysis of quenched fluids, yields accurate and precise free energy of formation data for the magnesian silicates.[14] This method is most useful in refractory silicate systems where the other components have much lower solubilities than silica. Measurements of silica solubility of zircon, according to the dissociation reaction

$$\underset{\text{zircon}}{ZrSiO_4} = \underset{\text{baddeleyite}}{ZrO_2} + SiO_2(aq) \tag{5}$$

should therefore, in principle, yield free energy data for reaction 1. In order to apply this method effectively, it is necessary to know accurately the activity coefficient–concentration relationship of solute silica at T and P high enough to achieve measurable solubility of zircon according to reaction 5. At low H_2O pressure, where silica solutions in equilibrium with refractory silicates are very dilute, an ideal solution approximation, in which SiO_2 activity is equal to its molar concentration, is quite adequate. At higher P and T, and consequently, higher silica solubilities, aqueous silica coexisting with refractory silicates and with quartz show substantial departure from ideal behavior, with silica activity coefficient, γ_s, progressively smaller than unity as silica mole fraction, X_s, increases. A recent experimental measurement of the γ_s–X_s relationship at 800°C and 1.2 GPa H_2O pressure over a large range of SiO_2 concentration[15] makes feasible a precise determination of the free energy of formation of zircon from its oxides.

II. Experimental Procedure

Aqueous solubility measurements on synthetic zircon crystals were carried out in H_2O at 800°C and 1.2 GPa. The weight change associated with zircon dissolution and regrowth in 30–40 mg of H_2O proved to be detectable to high precision. Weight changes can be ascribed entirely to the silica solution corresponding to reaction 5 because thermodynamic calculations predict that ZrO_2 solubility is below detection at the same P and T.

We used flawless, translucent, euhedral single crystals grown by a flux-melt method using lithium molybdate (Fig. 1(a)).[16–19] Refined lattice constants from powder X-ray diffraction are presented in Table II. The mean ZrO_2 concentration of the zircon crystals (100 analyses of random spots on zircon crystals

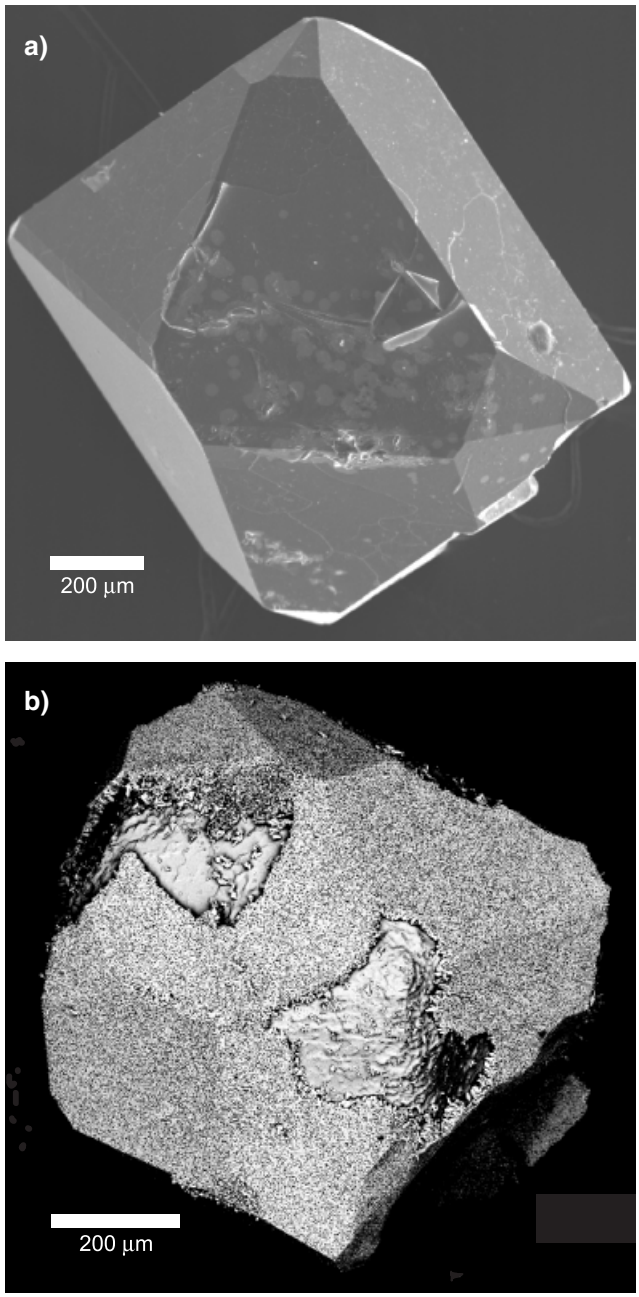

Fig. 1. Scanning-electron photomicrograph of synthetic zircon crystal (a) and baddeleyite-coated zircon (experiment #4, Table III) (b). In (b), portions of fine-grained ZrO_2 coat are broken away. Secondary electrons.

Table II. X-Ray Diffraction and Crystallographic Data for Synthetic Zircon

a (Å)	c (Å)	Volume (Å^3)	Density (g/cm^3)	Source
6.6102(8)	5.986(1)	261.57(6)	4.655	Finch *et al.*[20]
6.6070(1)	5.9835(1)	261.190(8)	4.660	Present study (R)
6.6078(2)	5.9831(2)	261.24(1)	4.661	Present study (P)

Errors are 1σ in last significant digit. (R) indicates results of Rietveld refinement;[21] (P) indicates results of lattice refinement from peak-profile fits.[22]

measured by electron microprobe) is 67.09% (16.65 mol% Zr), and the mean SiO_2 content is 32.79% (16.68 mol% Si). The expected stoichiometric values are 67.22% ZrO_2 (16.67 mol% Zr) and 32.78% SiO_2 (16.67 mol% Si). The small differences from the expected values are within the analytical uncertainty (0.18% RSD for Zr, 0.1% RSD for Si) of the analyses. Secondary ion mass spectrometry analyses of a randomly selected zircon crystal ($n = 3$) detected minor amounts of P (122 ppm), Li (0.12 ppm), and Mo (2.0 ppm).

Two to five zircon crystals were loaded into segments of Pt tubes of 3 mm length and 0.5 mm diameter. The tubes were lightly crimped at the ends, and some were additionally punctured with small holes to allow better access of the fluid. The small zircon-bearing capsules were sealed with about 32 mg of deionized H_2O by arc welding in a larger Pt tube segment. Runs of 70–112 h duration were made in a piston-cylinder apparatus with NaCl pressure medium and graphite heater sleeve.[23] Temperature and pressure uncertainties were, respectively, ±3°C and 0.3 kbar. At the end of each run, inner capsules were extracted and weighed. Weight losses of the inner capsules determined the solubilities. In one experiment (ZR-20), the inner capsule welded slightly to the outer capsule. In this case, solubility was determined from the weight change of the crystal itself. Weighing was carried out on a Mettler M3 microbalance, with $1\sigma = 2$ μg. The precise determination of weight changes at the microgram level propagates to tight constraints on thermochemical properties.

III. Results

Results are given in Table III. After experiments, the zircon crystals had a tightly adhering layer of fine-grained baddeleyite, but retained their original tetragonal crystal morphology (Fig. 1(b)). Reversal experiments (ZR-11, ZR-14) were performed by reloading the baddeleyite-coated zircons from experiments ZR-4 and ZR-12 (Table III) in an inner Pt capsule, which was sealed with H_2O and a small quartz crystal into an outer Pt container. The weight of the quartz crystal was chosen so that the fluid was initially slightly silica oversaturated with respect to zircon, as determined by the forward solubility experiments. Quartz dissolution is rapid (<2 h) compared with that of refractory silicates;[24] this assures that a state of silica oversaturation initially prevailed. The reversal experiments yielded patchy resorption of the baddeleyite layer, with weight gains consistent with zircon regrowth.

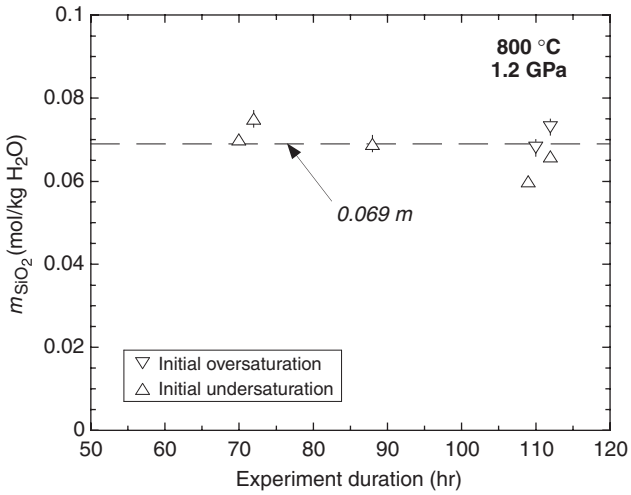

Fig. 2. SiO_2 molalities in the presence of zircon and baddeleyite at 800°C, 1.2 GPa, as a function of run duration. Upward and downward pointing triangles denote approach to equilibrium from initial under- and supersaturation (see text). Mean of six measurements (0.069 molal) shown with dashed line.

Runs of ≥70 h were sufficient to achieve equilibrium SiO_2 solute concentrations coexisting with zircon and baddeleyite (reaction 5), as indicated by the close approach of measured weight changes from opposite directions (Fig. 2). No crystalline residues were observed in the outer capsules, assuring no leakage of particulate matter, and that there was no vapor transport and regrowth of crystals of zircon or baddeleyite that could compromise the weight loss data. The only visible residues were transparent films of isotropic material inferred to be a quenched gel of SiO_2 and H_2O. The mean SiO_2 molality and mole fraction are, respectively, 0.069±0.010 and 0.00143±0.00019. The 2σ errors in the means of seven experiments are larger than those for individual runs because the latter account only for weighing uncertainty.

IV. Discussion

(1) Derivation of ΔG_f° of Zircon at 298 K, 10^5 Pa, from Solubility Measurements

The Gibbs free energy change of reaction 1 at a fixed P and T is given from solubility measurements by

$$\Delta G^\circ_{(1)} = RT \ln\left(\frac{a_s^{ZB}}{a_s^{Q}}\right) = RT \ln\left(\frac{\gamma_s^{ZB} X_s^{ZB}}{\gamma_s^{Q} X_s^{Q}}\right) \quad (6)$$

where a_s, γ_s and X_s are the activity, activity coefficient, and mole fraction of total dissolved silica corresponding to zircon–baddeleyite (ZB) or quartz (Q) equilibrium. The activity coefficients account for polymerization of aqueous silica.[15,24–27] A quantitative activity model has been experimentally calibrated for

Table III. Experimental Results, 800°C, 1.2 GPa

Experiment no.	Starting material	Time (h)	Wt H_2O (mg)	Start wt† (mg)	Extra Q (mg)	End wt† (mg)	m_{SiO_2} (mol/kg)	$10^3 X_{SiO_2}$	Reaction direction‡
ZR-4	Z	109	32.967	70.303		70.185	0.060(1)	1.08(2)	↑
ZR-11	ZBQ	110	32.676	66.027	0.172	66.065	0.068(2)	1.22(4)	↓
ZR-12	Z	112	32.877	68.030		67.899	0.066(1)	1.19(2)	↑
ZR-14	ZBQ	112	33.157	69.154	0.188	69.196	0.073(2)	1.31(4)	↓
ZR-17	ZQ	88	32.775	66.533	0.085	66.483	0.069(2)	1.24(4)	↑
ZR-18	Z	70	34.056	66.432		66.289	0.070(1)	1.26(2)	↑
ZR-20	ZQ	72	32.768	2.605	0.042	2.500	0.075(2)	1.35(4)	↑

B, baddeleyite; Q, quartz (single crystal, in outer capsule); Z, zircon. †All start and end weights are capsule+charge except ZR-20, in which the zircon crystal was weighed directly. Parenthetical numbers are uncertainties in last significant figure from 1σ weighing uncertainties (2 μg). ‡Downward-pointing and upward-pointing arrows denote equilibrium approached from high and low concentration, respectively.

homogeneous equilibrium among aqueous silica monomers (m) and dimers (d) in the fluid phase[15]

$$2SiO_{2(m)} = Si_2O_{4(d)} \quad (7)$$

Adopting a standard state for $SiO_{2,\ total}$ of unit activity of the hypothetical solution of unit mole fraction of monomers and a reference state of infinite dilution, and assuming an ideal solution of monomers and dimers with H_2O, the equilibrium constant, K, for Eq. (7) is

$$K = \frac{X_d}{X_m^2} \quad (8)$$

where X_d and X_m are the mole fraction of total dissolved silica occurring, respectively, as dimers and monomers, and mass balance requires that $X_s = X_m + 2X_d$. Equation (8) assumes that non-ideality of solute SiO_2 results entirely from the formation of dimers. This leads to

$$\gamma_s^B = \frac{-1 + (1 + 8KX_s^B)^{1/2}}{4KX_s^B} \quad (9)$$

where B denotes the ZB or quartz (Q) silica-activity buffers. For a given value of K (i.e., a fixed P and T), Eq. (9) describes the relationship between γ_s^B and X_s^B from $X_s^B = 0$ to quartz saturation.[15] Under the conditions of the present experiments (800°C, 1.2 GPa), $K = 116$–180 (Newton and Manning[15]), with equal probability of any value within this range. This is in excellent agreement with $K = 129 \pm 29$ from *in situ* Raman spectroscopy at the same P and T.[25] Solving Eq. (9) using the midpoint of $K = 148$ and $X_s^Q = 0.0248$ from Newton and Manning[15] gives $\gamma_s^Q = 0.307 \pm 0.028$. Similarly, X_s^{ZB} measured in the present study yields $\gamma_s^{ZB} = 0.778 \pm 0.008$ (Fig. 3).

Evaluation of Eq. (6) yields $\Delta G^\circ_{(1)}$ at 1.2 GPa, 1073 K, of -18.47 ± 1.16 kJ/mol. Volume, expansivity, and compressibility data[9] and thermal functions[6] give ΔG°_f of zircon from the oxides at 298 K, 10^5 Pa, of -19.30 ± 1.16 kJ/mol, where uncertainty from the thermophysical parameters is ignored.

(2) Comparison with Previous Estimates

Comparison of the present value of the free energy of formation of zircon with previous estimates based on experiments is given in Table I. Rosén and Muan[3] derived high-T $\Delta G^\circ_{(1)}$ values, with an estimated "accuracy of ± 0.1 kcal." However, the variation in $\Delta G^\circ_{(1)}$ with T implies heat content and entropy of reaction 1 that is inconsistent with other data.[6] To circumvent this problem, $\Delta G^\circ_{(1)}$ was taken to be the midpoint of the reported range (at 1273°C), and it was assumed that there is uniform distribution of possible $\Delta G^\circ_{(1)}$ between the minimum and maximum values associated with the full T range (1180°–1366°C). This yields 298 K, 10^5 Pa, $\Delta G^\circ_{(1)} = -20.79 \pm 1.16$ kJ/mol (Table I). The estimate of uncertainty is higher than that for individual measurements because the data set is treated as a single constraint to account for the entropy discrepancy. However, 2σ of 1.16 kJ/mol is an artifact of the narrow T interval of the original experiments; it would be larger if the T range had been larger assuming the same trend in the data. It is also possible that there was Co substitution in zircon,[6] which would raise additional accuracy concerns.

Schuiling *et al.*[4] derived a wide bracket on $\Delta G^\circ_{(1)}$ at 0.1 GPa, 1000 K. Correction to 10^5 Pa, 298 K, using equations and data for volume change[9] and thermal functions[6] gives -24.28 ± 4.49 kJ/mol. The 2σ uncertainty reflects equal probability of $\Delta G^\circ_{(1)}$ within the bracket, but this uncertainty should be considered a minimum because uncertainties in the thermodynamic properties of phases participating in the studied equilibria were not included. The experimental study[5] of reaction 4 can be used in conjunction with data from Holland and Powell[9] to calculate $\Delta G^\circ_{(1)} = -18.44 \pm 1.71$ kJ/mol (Table I). As above, the 2σ reflects only the width of the experimental bracket; it does not take into account uncertainties in thermodynamic properties of additional phases. Finally, Ellison and Navrotsky[6] give $\Delta G^\circ_{(1)} = -23.57$ kJ/mol at 298 K, 10^5 Pa. Based on six measurements of enthalpy of solution, they report a 95% confidence interval of ± 3.62 kJ/mol.

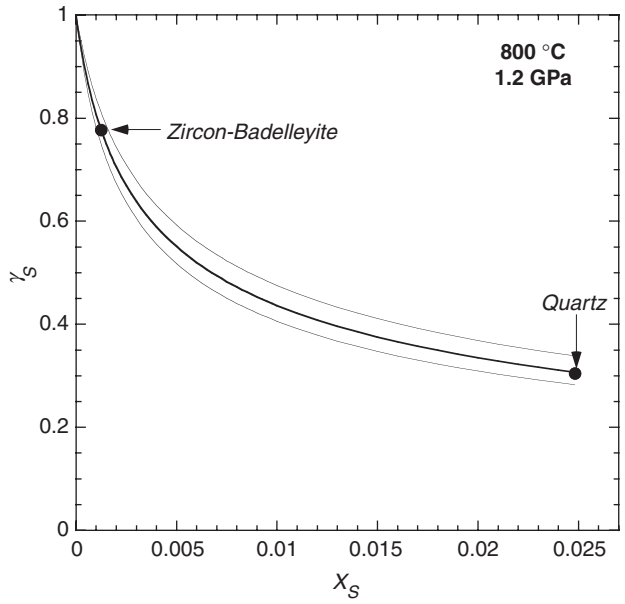

Fig. 3. Activity coefficient of aqueous silica (γ_s) from Eq. (9), text, as a function of mole fraction of aqueous silica (X_s). The bold curve was calculated using $K = 148$; the thin curves correspond to 2σ in K of 32 (Newton and Manning[15]). Values of γ_s are shown for experimentally determined X_s in equilibrium with quartz and zircon-baddeleyite.

Table I shows that the newly derived ΔG°_f of zircon from the oxides of -19.30 ± 1.16 kJ/mol is at the low end of the values derived from previous studies. It is most consistent with the result of Ferry *et al.*[5] More significantly, comparison of uncertainties due strictly to experimental determinations (Table I) shows that the present result has a precision equal to the best previously obtained.[3] Because the uncertainty in that value is probably underestimated because of the narrow T range of measurement, the present result can be considered the most precise determination to date.

Table I also lists standard free energy of formation data for zircon from its oxides at 298 K, 10^5 Pa, from several compilations of thermochemical data. Of these estimates, that of Chase *et al.*[7] is clearly significantly less negative than, and inconsistent with, the present result, and all previous experimental studies.[6] The reason for the systematically less negative value in the other data sets, as compared with early experimental studies, is not clear. Holland and Powell[9] cite Robie and Hemingway,[8] who in turn cite Schuiling *et al.*[4] and Ellison and Navrotsky[6] as sources for the Gibbs energy of formation of zircon. Given the large uncertainties in these latter studies, the agreement must be at least in part fortuitous.

V. Applications

Solubility measurements at high P and T have proven feasible for determining the free energy of formation of a refractory silicate because of the great increase in silica solubility with pressure above 0.5 GPa H_2O pressure. The greatest challenge in refining this method as a general tool will be a more accurate definition of the activity coefficient of solute silica over a broad range of temperature and pressure. This may be achieved through detailed solubility studies on other silica-buffering assemblages, such as kyanite (Al_2SiO_5)–corundum (Al_2O_3) and rutile (TiO_2)–forsterite (Mg_2SiO_4)–geikielite ($MgTiO_3$).[15]

Other refractory silicates whose free energies of formation are at present poorly known could be studied by methods of the present study. Examples include titanite ($CaTiSiO_5$) with perovskite ($CaTiO_3$), cordierite ($Mg_2Al_4Si_5O_{18}$) with spinel ($MgAl_2O_4$), and sillimanite (Al_2SiO_5) with corundum. The last two systems offer the possibility of studying the effects on free energy of Al–Si order–disorder. It is possible that the degree of metamict structural degradation in natural zircon from α recoil, which is an important quantity for interpretation of geochronologic data, could be addressed by determining the solubility difference between damaged and undamaged zircon crystals, in conjunction with structural study.[28,29]

Acknowledgments

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