

Gibbs energies of formation of zircon (ZrSiO_4), thorite (ThSiO_4), and phenacite (Be_2SiO_4).

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Abstract

Zircon, thorite, and phenacite are very refractory compounds which do not yield to solution calorimetry. In order to obtain approximate Gibbs energies of formation for these minerals, their reactions with a number of silica-undersaturated compounds (silicates or oxides) were studied. Conversely baddeleyite (ZrO_2), thorianite (ThO_2), and bromellite (BeO) were reacted with the appropriate silicates. As the Gibbs energies of reaction of the undersaturated compounds with SiO_2 are known, the experiments yield the following data: $\Delta G_{298, 1 \text{ bar}}^0 = -459.02 \pm 1.04$ kcal for zircon, -489.67 ± 1.04 for thorite, and -480.20 ± 1.01 for phenacite.

Introduction

Solution calorimetry is of little value to obtain the enthalpies of formation of zircon, thorite, and phenacite because of their refractory nature. It was decided, therefore, to carry out a number of experiments of the kind



As the Gibbs energy of the reaction $\text{CaTiO}_3 + \text{SiO}_2 \rightarrow \text{CaTiSiO}_5$ is known ($= -7.1$ kcal), whether the Gibbs energy for the reaction $\text{ZrO}_2 + \text{SiO}_2 \rightarrow \text{ZrSiO}_4$ will be larger or smaller than -7.1 kcal depends on the direction in which the first reaction proceeds. An essentially similar approach was used by Schuiling and Vink (1967), in their determination of the Gibbs energy of formation of sphene.

By repeating the procedure with different silicates or oxides, for which the Gibbs energies for the silication reactions are known, it is possible to determine an interval for the Gibbs energies of reaction of ZrO_2 , ThO_2 , and BeO with SiO_2 in forming their respective silicates.

Experimental

For these experiments the synthetic compounds or natural starting materials listed in Table 1 were used. A microprobe analysis of the natural olivine gave $(\text{Mg}_{0.91}\text{Fe}_{0.09})_2\text{SiO}_4$, and of the enstatite, $(\text{Mg}_{0.98}\text{Fe}_{0.02})\text{SiO}_3$.

Table 2 lists the Gibbs energies of reaction for the reactions involved in this study. Inasmuch as the experiments were carried out at 1000 K and 1 kbar, the thermodynamic data at 1000 K, 1 atm as tabu-

lated by Robie and Waldbaum (1968) were corrected for pressure, neglecting the temperature dependence of ΔV , by means of the formula

$$\Delta G_{(P, 1000 \text{ K})} = \Delta G_{(1 \text{ atm}, 1000 \text{ K})} + P\Delta V_{(298 \text{ K})} \quad (1)$$

The forsterite and enstatite used in the experiments are considered to be ideal solid solutions between respectively forsterite and fayalite, and enstatite and ferrosilite. The Gibbs energy of formation of ferrosilite at 1000 K, 1 kbar was calculated by means of the data of Lindsley (1965) and Lindsley *et al* (1963). The unit cell parameters of the albite, kept at 1000 K and 1 kbar ($P_{\text{H}_2\text{O}}$) during at least two weeks, are in good agreement with those of high albite as given by Waldbaum (1968).

The experimental procedure was as follows. Stoichiometric mixtures of ZrO_2 , ThO_2 , or BeO with the reactants on the right hand side of Table 2, and mixtures of ZrSiO_4 , ThSiO_4 , or Be_2SiO_4 with the reactants (without quartz) on the left hand side of Table 2 were used as starting material. Approximately 100 mg of these mixtures, to which 10 mg H_2O was added, were put in gold capsules of 2 cm length and 2.8 mm ϕ .

The gold capsules were welded shut and put into standard $\frac{1}{4}$ " inner diameter cold seal vessels (Ulmer, 1971). The vessels were run in the vertical upside down position, in which the gold capsules are kept at the hot spot by supporting filler rods. The pressure medium was argon. Run duration varied between 2 and 12 weeks (see Table 3). As the experiments are solid-solid reactions of the go-, no-go type, temperature and pressure control is not of critical

TABLE 1. Compounds Used in the Experiments

Compound	Chemical Formula	Abbreviation	Locality
forsterite	Mg ₂ SiO ₄	fo	Naxos, Greece
enstatite	MgSiO ₃	en	Bamle, Norway
nepheline	NaAlSi ₃ O ₈	nef	synthetic
albite	NaAlSi ₃ O ₈	ab	Amelia, Virginia U.S.A.
perovskite	CaTiO ₃	pvs	synthetic
sphene	CaTiSiO ₅	sph	Ontario, Canada
leucite	KAlSi ₂ O ₆	lc	synthetic
K-feldspar	KAlSi ₃ O ₈	kf	Laacher See, West Germany
zincite	ZnO	zn	synthetic
willemite	Zn ₂ SiO ₄	wil	Aachen, West Germany
baddeleyite	ZrO ₂	bad	synthetic
zircon	ZrSiO ₄	zr	North Carolina U.S.A.
bromellite	BeO	bro	synthetic
phenacite	Be ₂ SiO ₄	phen	Kragerö, Norway
thorianite	ThO ₂	thn	synthetic
thorite	ThSiO ₄	th	synthetic

importance, as it is in equilibrium experiments. A combination of all possible errors and frequent checks showed that temperature variation was less than 10°C, in most cases less than 5°, whereas pressure variations were commonly less than 50 bars.

After termination of the runs these were quenched, and after a control weighing for possible leakage during the run, the run products were analyzed by X-ray diffraction with a 4-sample Nonius-Guinier camera. This set-up has a better detection limit than diffractometry, and permits a direct comparison of starting material and run products. Although none of the samples had reacted to completion, in all cases the direction of the reaction could be determined unambiguously. No inconsistent results were obtained; *i.e.*, if a certain mixture showed a reaction, the

TABLE 2. Gibbs Energies of Reaction of the Relevant Reactions at 1000 K, 1 kbar

<1> fo _{0.91} fa _{0.09} + qtz → 2 en _{0.91} fs _{0.09}	-1.37 kcal
<2> fo _{0.98} fa _{0.02} + qtz → 2 en _{0.98} fs _{0.02}	-1.55 kcal
<3> ½ nef + qtz → ½ ab	-3.42 kcal
<4> pvs + qtz → sph	-5.28 kcal
<5> lc + qtz → kf	-5.56 kcal
<6> 2 zn + qtz → wil	-7.62 kcal

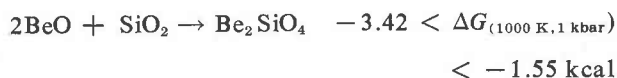
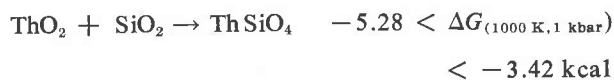
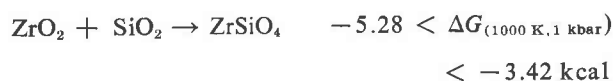
TABLE 3. Results of Experiments at 1000 K, 1 kbar

Starting Material	Products	Run Duration (weeks)
zr + lc	bad + kf + zr + lc	3
bad + kf	bad + kf	3
zr + zn	bad + wil + zr + zn	3
bad + wil	bad + wil	3
zr + nef	zr + nef	12
bad + ab	zr + nef + bad + ab	12
zr + pvs	bad + sph + zr + pvs	3
bad + sph	bad + sph	3
zr + fo	zr + fo	12
bad + en	zr + fo + bad + en	12
thn + kf	thn + kf	2
thn + wil	thn + wil	2
thn + sph	thn + sph	2
th + pvs	thn + sph + th + pvs	2
th + fo	th + fo	2
thn + en	th + fo + thn + en	12
th + nef	th + nef	2
thn + ab	thn + ab	2
thn + ab	th + nef + thn + ab	12
bro + sph	bro + sph	4
phen + pvs	bro + sph + phen + pvs	3
bro + kf	bro + kf	3
bro + en	phen + fo + bro + en	4
phen + fo	phen + fo	3
bro + ab	bro + ab	3
phen + nef	bro + ab + phen + nef	3

reverse reaction was never observed. Table 3 summarizes the results of all the experiments.

Discussion of results

By combining the data of Table 2 with the results obtained in Table 3 it can be seen that



These values must be converted to values at 298 K and 1 bar. The pressure correction for all three reac-

TABLE 4. Gibbs Energies of Formation of Zircon, Thorite, and Phenacite

Substance	$\Delta G_{(298 \text{ K}, 1 \text{ atm})}^o$
zircon (ZrSiO ₄)	-459.02 ± 1.04 kcal
thorite (ThSiO ₄)	-489.67 ± 1.04 kcal
phenacite (Be ₂ SiO ₄)	-480.20 ± 1.01 kcal

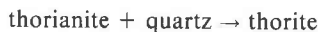
tions was done by means of Equation (1), as all the molar volumes of the participating solids are known. To correct for temperature, if the temperature dependences of the ΔS were known, one should use, according to Robie (1965), the formula

$$\Delta G^\circ_T = \Delta H^\circ_{298} + T\Delta \frac{(G^\circ_T - H^\circ_{298})}{T} \quad (2)$$

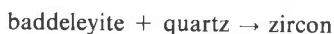
As a matter of fact, these data are not available for any phases except those in the zircon reaction, which was treated accordingly. For thorite and phenacite the data were reduced by means of the formula

$$\Delta G^\circ_{T,P} = \Delta G^\circ_{298,P} - \Delta S(T - 298) \quad (3)$$

in which the temperature dependence of ΔS is neglected. An additional difficulty arose with thorite because its entropy is not known. We have thus assumed that the entropy of reaction of

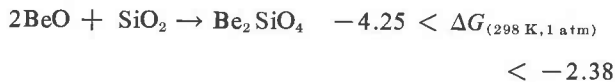
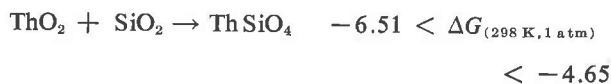
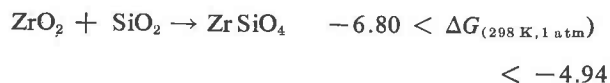


would be the same as for the reaction



because the participating phases in both cases are crystallographically similar.

The reduction of the thermodynamic data at 1000 K and 1 kbar to standard conditions by means of Equations (1) and (2), or (1) and (3), leads to the following results:



The combination of these data with the thermodynamic data for the simple oxides leads to the results of Table 4.

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References

- LINDSLEY, D.H. (1966) Pressure-temperature relations in the system FeO-SiO₂. *Carnegie Inst. Wash. Year Book*, **65**, 226-230.
- , I.D. MACGREGOR, AND B. T. C. DAVIS (1964) Synthesis and stability of ferrosilite. *Carnegie Inst. Wash. Year Book*, **63**, 174-178.
- ROBIE, R. A. (1965) Heat and free energy of formation of herzenbergite, troilite, magnesite, and rhodochrosite calculated from equilibrium data. *U.S. Geol. Surv. Prof. Pap.* **525 D**, D65-D72.
- , AND D. R. WALDBAUM (1968) Thermodynamic properties of minerals and related substances at 298.15 K (25°C) and 1 atmosphere (1.013 bars) pressure and at higher temperatures. *U.S. Geol. Surv. Bull.* **1259**.
- SCHUILING, R. D., AND B. W. VINK (1967) Stability relations of some titanium-minerals (sphene, perovskite, rutile, anatase). *Geochim. Cosmochim. Acta*, **31**, 2339-2411.
- ULMER, G. C. (1971) *Research Techniques for High Pressure and High Temperature*. Springer-Verlag, Berlin-Heidelberg-New York.
- WALDBAUM, D. R. (1968) High-temperature thermodynamic properties of alkali feldspars. *Contrib. Mineral. Petrol.* **17**, 71-77.

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