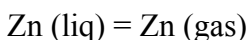


Thermochemical data for zinc and its compounds in the MAGMA code
Bruce Fegley December 2012

Zn (c, liq, gas) – JANAF data were used (Chase 1998). The data for Zn (c, liq) extend to 2000 K, those for the gas to 6000 K. Zinc metal is the reference state up to the melting point of 692.677 K, Zn (liquid) is the reference state between the melting point of 692.677 K and the boiling point of 1180.173 K, and Zn (g) is the reference state at higher temperatures. The equations for vaporization of liquid zinc are



$$\log_{10}K \text{ (bar)} = 5.1892 - 6,124.14/T$$

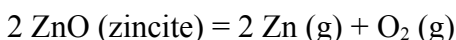
This equation gives a one bar boiling point of 1180.170 K, in almost exact agreement with the 4th edition JANAF Tables.

ZnO (zincite, liquid) – The standard enthalpy of formation at 298 K ($-350.46 \text{ kJ mol}^{-1}$) is from Robie and Hemingway (1995). The standard entropy at 298 K ($43.639 \text{ J mol}^{-1} \text{ K}^{-1}$) and the heat capacity is from Jak et al (1997). The melting point (2248 K), enthalpy of melting ($\sim 54.3 \text{ kJ mol}^{-1}$), and heat capacity of the liquid ($60.668 \text{ J mol}^{-1} \text{ K}^{-1}$) are all from Jak et al. (1997). The equation

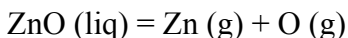
$$\log_{10}K = -1.21684 + 2746.417/T$$

was used for converting data from ZnO (zincite) to ZnO (liq) standard states. It gives a melting point of 2257 K, 9 degrees higher than the actual melting point.

Zincite vaporizes congruently to monatomic Zn gas and O₂ molecules (Anthrop and Searcy 1964)



We are interested in vaporization of molten ZnO to the atoms in the MAGMA code



$$\log_{10}K = 12.02455 - 33,554.102/T$$

ZnO (gas) – The standard enthalpy of formation at 298 K ($+220.180 \text{ kJ mol}^{-1}$) is based on the dissociation energy measured by Clemmer et al. (1991). This is supported by the measurements of Watson et al. (1993) that give a lower limit of 151 kJ mol^{-1} for the standard enthalpy at 298 K. The thermal functions for ZnO (g) are from Pedley and Marshall (1983) ($> 298 \text{ K}$) and $H_{298} - H_0 = 8.993 \text{ kJ mol}^{-1}$ is from Kelley and King (1961). Thermal functions for Zn (g) and O (g) are from JANAF.

Zn₂SiO₄ (willemite, liquid) – The phase diagram of Bunting (1930) shows this is the only stable zinc silicate. Zinc metasilicate (ZnSiO₃) is only stable above 3 GPa (Akaogi et. al. 1990) and its heat of formation given in Glushko is based on an apparently incorrect measurement by Mulert (1912 Z. Anorg. Allgem. Chem. 75, 198), and estimated thermal functions. Akaogi et al (1990) give a heat of formation, entropy, and heat capacity for ZnSiO₃ based on their calorimetric data.

The standard enthalpy of formation of willemite at 298 K (–1640.866 kJ mol^{–1}) is calculated from the standard enthalpy of formation from the oxides (–29.246 kJ mol^{–1}), which was determined by King (1951), and the standard enthalpies of formation of quartz (–910.7 kJ mol^{–1}) and zincite (–350.46 kJ mol^{–1}) from Robie and Hemingway (1995). The standard entropy at 298 K is also from Robie and Hemingway (1995). The (estimated) heat capacity and one bar melting point (1512 C) are from Kubaschewski and Alcock (1979). The melting point is essentially the same as that found by Bunting (1930). The estimated heat capacity in Kubaschewski and Alcock (1979) agrees within several percent (e.g., at 1000 K, 170.66 vs. 178.81 from our table) with the mean specific heat given by Egorov and Smirnova (1965). This is

$$c_p \text{ (cal/g K)} = 0.1596 + 2.47 \times 10^{-5}T - 1.27 \times 10^{-9}T^2 \text{ from 589-1587 K.}$$

The thermal functions (heat capacity, enthalpy, entropy) above the melting point are calculated using the same (estimated) equation from Kubaschewski and Alcock (1979). The calculated table gives Gibbs energy of reaction values from the oxides that agree with the work of Kitchener and Ignatowicz (1951) and Björkman (1986), e.g., at 1200 K, –28.7 kJ mol^{–1} (Kitchener & Ignatowicz) versus –29.3 kJ mol^{–1} from our table. The entropy of fusion is estimated as 7.9 ± 0.9 J/g-atom K, which is the mean of values in the table.

Mineral	m.p. (K)	ΔH_{fus} (kJ/mol)	ΔS_{fus} (J/g-atom K)	Reference
fayalite	1490	92.2	8.84	RB86
fayalite	1490	89.3	8.56	ibid
Mn ₂ SiO ₄	1620	89.5	7.89	ibid
Mn ₂ SiO ₄	1620	89.0	7.85	RH95
Pb ₂ SiO ₄	1016	55.3	7.78	RB86
Pb ₂ SiO ₄	1016	46.4	6.52	ibid
Co ₂ SiO ₄	1688	103	8.72	RH95
Mg ₂ SiO ₄	2163	102.8	6.79	RH95

This gives an entropy of fusion of 55.30 J/mol K and an enthalpy of fusion of about 98.7 ± 11.2 kJ mol^{–1} (the exact value of 98,710.5 J/mol was used in the calculations). For reference the mean entropy of fusion from Richard's Rule is 8.4 J/g-atom K, and the mean value is 8.8 ± 4.4 J/g-atom K for 150 elements, minerals, and inorganic compounds

(Fegley 2013 p. 198). The C_p for molten Zn_2SiO_4 was estimated in two ways. First, using the average of the C_p per gram atom for Fe_2SiO_4 (34.37 J/g-atom K, Kelley 1960), Mn_2SiO_4 (34.73 J/g-atom K, Robie et al 1978), and Mg_2SiO_4 (32.14 J/g-atom K, Tangeman et al 2001). This gives $C_p = 33.75$ J/g-atom K = 236.2 J/mol K. Second, using the partial molal C_p values of 92.57 J/mol K (ZnO) and 81.37 J/mol K (SiO_2) of Richet and Bottinga (1986) and the formula

$$C_p = 3[2/3ZnO + 1/3SiO_2]/7 = 38.07 \text{ J/g-atom K} = 266.5 \text{ J/mol K}$$

The selected value for the heat capacity of the liquid is the arithmetic mean of the two values = 251 J/mol K and is taken as constant above 1785 K.

A Hess' law thermochemical cycle using the heat contents of willemite, ZnO (liq, my table), and SiO_2 (liq, JANAF) gives 79.616 kJ/mol for the enthalpy difference between solid and melt at 298 K. A similar cycle using a constant C_p for Zn_2SiO_4 (liq) from 298 – 1785 K gives a much lower value of 11.689 kJ/mol which I think is unreasonable. Using the value of 79.616 kJ/mol, the derived standard enthalpy of formation at 298 K for Zn_2SiO_4 (liq) is –1561.250 kJ/mol. (These values are needed to make a table for Zn_2SiO_4 (liq), but were not used in computing the log K equation for formation of the liquid silicate from the constituent liquid oxides.)

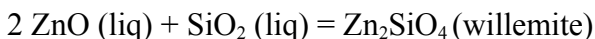
The standard Gibbs energy change for melting (ΔG°) was calculated using a temperature - dependent ΔC_p for melt – solid, taking the melting point as the reference temperature, and using the enthalpy and entropy of melting given above. The thermal functions for the solid are extrapolated above the melting point with the (estimated) heat capacity equation of Kubaschewski and Alcock (1979). A linear least squares fit to the data points at 1785, 1800, 1900, and 2000 K was adjusted to give $\Delta G^\circ = 0$ at 1785 K. This gives the equation below for G° (melt) – G° (solid):

$$\Delta G^\circ = 102,182.147 - 57.2449T \text{ J/mol}$$

The corresponding equation for log K of melting is

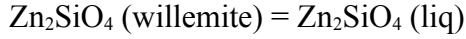
$$\log K = 2.990 - 5337.33/T$$

This was combined with the two equations below to give log K for formation of liquid Zn orthosilicate from the constituent liquid oxides:



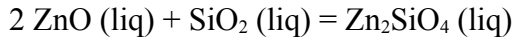
$$\log K = -2.394 + 7115.2/T$$

From my tables for ZnO (liq) and willemite and from the 3rd ed. JANAF Table for SiO_2 (liq), using data at 1500, 2000, and 2500 K. (No equation for SiO_2 melting is involved.)



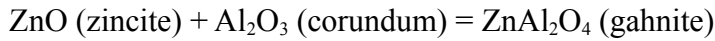
$$\log K = 2.990 - 5337.33/T$$

Note: Using a constant ΔC_p for melt – solid did not work – it gave values for the log K (liquid oxides → liquid silicate) equation that had showed the liquid silicate becoming more stable with increasing temperature, which cannot be true.



$$\log K = 0.596 + 1777.9/T$$

ZnAl₂O₄ (gahnite, liquid) – Jacob (1976) electrochemically measured the standard Gibbs energy of formation from the constituent oxides

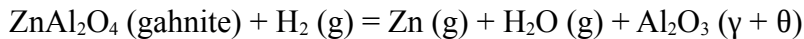


$$\Delta G^\circ = -10,750 + 1.57T \text{ cal/mol } (\pm 150 \text{ cal/mol})$$

$$T = 700 - 900 \text{ C } (973 - 1173 \text{ K})$$

His ΔH° of -10,750 calories is very similar to $\Delta H^\circ = -10,560$ calories measured at 700 C by Navrotsky and Kleppa (1968).

Gilbert and Kitchener (1956) also measured ΔG° for gahnite formation from the oxides, but metastable ($\gamma + \theta$) alumina instead of corundum may form in their H₂ reduction experiments



$$\Delta G^\circ = -14,120 (\pm 1700) + 1.17 (\pm 1.3) T \text{ cal/mol}$$

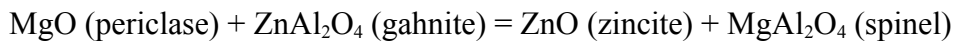
$$T = 787 - 1097 \text{ C } (1060 - 1370 \text{ K})$$

Within the uncertainties the two ΔS° values are identical but the ΔH° values are different.

Navrotsky (1986) gives the heat content ($H_{973} - H_{298}$) = 107 kJ/mol, which agrees very well (2% difference) with the value of 104.8 kJ/mol from the equation given by Kelley (1960)

$$C_p = 24.40 + 20.30 \times 10^{-3}T \text{ (cal/mol K) } 298 - 1298 \text{ K}$$

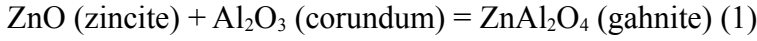
However I used my own heat capacity equation derived assuming $\Delta C_p = 0$ for



and using Maier-Kelley equations from Kelley (1960) for periclase, spinel, and zincite. My derived equation for gahnite is

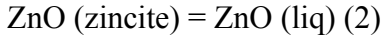
$$C_p(\text{ZnAl}_2\text{O}_4) = 38.33 + 5.88 \times 10^{-3}T - 10.48 \times 10^5/T^2 \text{ (cal/mol K)}$$

I adopt Jacobs' equation and combine it with data for melting ZnO and corundum to find the log K for formation of gahnite from its constituent liquid oxides.

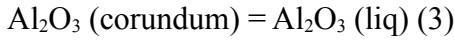


$$\Delta G^\circ = -10,750 + 1.57T \text{ cal/mol } (\pm 150 \text{ cal/mol})$$

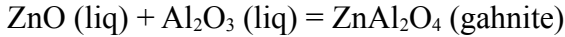
$$\log K_1 = -0.34311 + 2,349.35320/T$$



$$\log K_2 = 1.21684 - 2,746.417/T$$

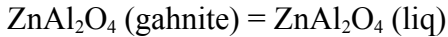


$$\log K_3 = 2.5252 - 5.875.4273/T$$



$$\log K_4 = \log K_1 - \log K_2 - \log K_3 = -4.0852 + 10,971.1975/T$$

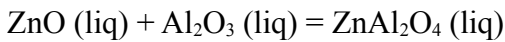
Hansson et al (2004) redetermined the ZnO – Al₂O₃ phase diagram of Bunting (1932). This shows that alumina-rich gahnite melts at 1950 C (2223 K). However, the liquidus is very flat and the melting point of stoichiometric gahnite is the same. The enthalpy of fusion (119,353 J/mol) was estimated using the average entropy of fusion of 7.67 ± 2.37 J/mol K for 41 oxides and silicates. The estimated heat capacity of the liquid (230.09 J/mol K) was estimated using the average heat capacity of 32.87 ± 3.37 J/g-atom K for 30 molten oxides and silicates. I derive the following equation for the melting reaction



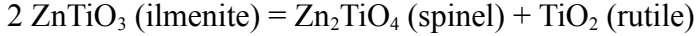
$$\log K = 2.80805 - 6,243.68536/T$$

Combining this with log K₄ above gives

$$\log K = -1.27715 + 4,727.51/T$$



ZnTiO₃ (ilmenite, liq) – Dulin & Rase (1960) determined the ZnO – TiO₂ phase diagram. They find that ZnTiO₃ (ilmenite) decomposes to TiO₂ (rutile) plus Zn₂TiO₄ (spinel) at 925 ± 25 °C (1198 ± 25 K) under dry conditions, i.e. ΔG = 0 for the reaction at 1198 K:



$$\Delta G = 0$$

All compounds are solid so the ΔV dP integral is zero and ΔG° = ΔG and

$$\Delta G^\circ = \Delta G^\circ(\text{TiO}_2, \text{rutile}) + \Delta G^\circ(\text{Zn}_2\text{TiO}_4, \text{spinel}) - 2 \Delta G^\circ(\text{ZnTiO}_3, \text{ilmenite}) = 0$$

$$\Delta G^\circ(\text{ZnTiO}_3, \text{ilmenite}) = \frac{1}{2} \Delta G^\circ(\text{Zn}_2\text{TiO}_4, \text{spinel})$$

(All ΔG° values are reference to oxides, so that for rutile is zero).

Using my selected values for Zn₂TiO₄, spinel at 1200 K (see below),

$$\Delta G^\circ(\text{ZnTiO}_3, \text{ilmenite}) = \frac{1}{2} \Delta G^\circ(\text{Zn}_2\text{TiO}_4, \text{spinel}) = \frac{1}{2} (-15,319 \text{ J/mol}) = -7,660 \text{ J/mol}$$

Jacob & Alcock (1975) made emf measurements from 930 – 1100 K that give

$$\Delta G^\circ(\text{ZnTiO}_3, \text{ilmenite}) = -1600 - 0.199T (\pm 50 \text{ cal/mol})$$

Extrapolating their equation to 1200 K and converting to J/mol gives

$$\Delta G^\circ(\text{ZnTiO}_3, \text{ilmenite}) = -7,694 \text{ J/mol}$$

This is identical to the value derived from the phase diagram within the uncertainty of the emf data (± 209 J/mol).

In contrast, at 1323 K the phase equilibrium data of Navrotsky & Muan (1970) give

$$\Delta G^\circ(\text{ZnTiO}_3, \text{ilmenite}) = +7,100 \text{ J/mol}$$

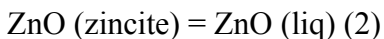
Recalculating this value using more recent data for ΔG°(NiTiO₃, ilmenite) from Jacob et al. (2007) gives ~ -27,000 for formation of ZnTiO₃ from the oxides at 1323 K. I conclude the phase equilibrium data of Navrotsky & Muan cannot be used to derive data for the Gibbs energy of ZnTiO₃ (ilmenite).

Instead I extrapolated the equation of Jacob & Alcock (1975) to higher temperatures and used it to calculate log K for forming ZnTiO₃ (ilmenite) from the constituent liquid oxides as follows.



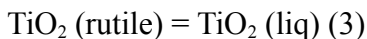
$$\log K_1 = 0.04349 + 349.673/T$$

This is from the Gibbs energy equation of Jacob & Alcock (1975)



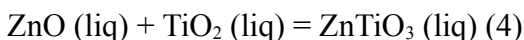
$$\log K_2 = 1.21684 - 2,746.417/T$$

This is from my sigmaplot fit in the “Chemistry of the Moon-forming Impact” directory on Dropbox.com.



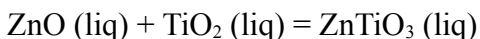
$$\log K_3 = 1.5329 - 3,228.8/T$$

This is from my calculations done on 12/3/12 and is a fit to log K at 1500, 2000, and 2500 K. I just checked this (12/13/12) against log K at 2000 – 2300 K calculated from the 3rd edition of the JANAF Tables and there is agreement within 5% or better (slightly different fits using different T-ranges). Adding together the log K values for these three reactions gives the log K value for the desired 4th reaction, forming ZnTiO₃ (ilmenite) from its constituent liquid oxides.



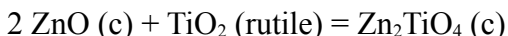
$$\log K_4 = 2.793 - 5,625.544/T$$

The log K = 0 at ~ 2014 K for this reaction – equal stability of the liquid oxides and ilmenite. I take this as the fictive congruent melting point of ZnTiO₃ (ilmenite). This is close to the ~ 2000 K liquidus temperature of the BSE magma, so ZnTiO₃ (liq) is only slightly less stable than the solid at lower temperatures and conversely the solid is only slightly less stable than the liquid at higher temperatures. I thus approximate the data for the liquid using that of the solid and the final (rounded off) equation is



$$\log K = 2.79 - 5625/T$$

Zn₂TiO₄ (spinel, liq) – Todd & Kelley (1956) measured the heat of formation from the oxides:



$$\Delta H^\circ = -1,500 \pm 250 \text{ cal/mol } 298 \text{ K}$$

Navrotsky and Kleppa (1968) measured $\Delta H^\circ = -830 \pm 160 \text{ cal/mol}$ at 970 K from molten oxide calorimetry. Their value corresponds to $\Delta H^\circ(\text{oxides}) = -1,641 \text{ cal/mol}$ ($-6,868 \text{ J/mol}$) at 298 K using heat contents of 32.246 kJ/mol (ZnO), 46.339 kJ/mol for rutile, and 114.226 kJ/mol for Zn orthotitanate. My calculated standard enthalpies of formation from the elements ($-1651.943 \text{ kJ mol}^{-1}$ and $-1652.535 \text{ kJ mol}^{-1}$) use the standard enthalpy of formation of zincite ($-350.46 \text{ kJ mol}^{-1}$) from Robie and Hemingway (1995) and of rutile ($-944.747 \pm 1.3 \text{ kJ mol}^{-1}$) from JANAF 4th edition (Chase 1998). My selected value for the standard enthalpy of formation from the elements at 298 K is the unweighted mean rounded to $-1,652.240 \text{ kJ/mol}$.

King (1955) measured $S^\circ_{298} - S^\circ_{51} = 30.75 \text{ cal/mol K}$ and used a mixture of Debye and Einstein functions to compute $S^\circ_{51} - S^\circ_0 = 2.07 \text{ cal/mol K}$ giving $S^\circ_{298} = 32.8 \pm 0.2 \text{ cal/mol K}$. This is the thermal (or lattice) entropy. However, zinc orthotitanate is an inverse spinel and should have a configurational entropy of $2R(\ln 2) = 2.755 \text{ cal/mol K}$ (11.526 J/mol K) for completely random cation mixing. Kelley and King (1961) added a configurational entropy of $1.4 \text{ cal/mol K} \sim R(\ln 2)$ to King's value and list $34.2 \pm 0.3 \text{ cal/mol K}$ (143.093 J/mol K). Their configurational entropy is only half that expected for completely random mixing. Jacob and Alcock (1975) made emf measurements that give

$$\Delta G^\circ = -750 - 2.46T \text{ cal/mol } (\pm 75 \text{ cal/mol})$$

$$T = 930 - 1100 \text{ K}$$

Navrotsky and Muan (1970) derived $\Delta G^\circ = -4.7 (\pm 0.6) \text{ kcal/mol}$ at 1050 C (1323 K) from activity – composition measurements on the $\text{Co}_2\text{TiO}_4 - \text{Zn}_2\text{TiO}_4$ solid solution. The equation of Jacob and Alcock gives -4005 cal/mol at 1323 K and my final data table gives -4036 cal/mol at 1323 K.

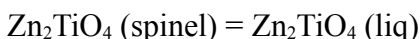
The data of Jacob and Alcock (1975) imply incomplete cation mixing corresponding to 1.90 cal/mol K [$7.950 \text{ J/mol K} \sim 1.38R(\ln 2)$] at 930 – 1100 K. Oxygen-17 magic angle spinning NMR measurements by Millard et al. (1995) show that Zn orthotitanate is an inverse spinel above 561 C (834 K) with no Ti cations in the tetrahedral site. Both normal and inverse spinel structures were observed at lower temperatures. The $\Delta G^\circ(\text{oxide})$ value at 1000 K from Jacob and Alcock (1975) is reproduced almost exactly with the selected thermodynamic data (298 K heat of formation and entropy, and Cp fits described below).

Several different C_p fits that reproduce the data of Bonnickson (1955) were used for the Zn orthotitanate table and the equation for the highest T range was extrapolated above the

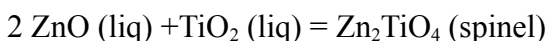
melting point to compute ΔG° (melt – solid) as a function of temperature. Kelley's (1960) C_p equation is

$$C_p = 39.82 + 5.54 \times 10^{-3}T - 7.69 \times 10^5/T^2 \text{ cal/mol K } 298 - 1800 \text{ K}$$

This was not used to make the table. The melting point of Zn orthotitanate = $1549 \pm 20^\circ \text{C}$ ($1822 \pm 20 \text{ K}$) based on the phase diagram of Dulin and Rase (1960). The enthalpy of fusion ($97,823 \text{ J/mol}$) was estimated using the average entropy of fusion of $7.67 \pm 2.37 \text{ J/mol K}$ for 41 oxides and silicates. The estimated heat capacity of the liquid (230.09 J/mol K) was estimated using the average heat capacity of $32.87 \pm 3.37 \text{ J/g-atom K}$ for 30 molten oxides and silicates. My results for melting of Zn orthotitanate are



$$\log K = 2.8881 - 5,262.2017/T$$



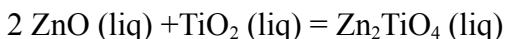
$$\log K = -3.0345 + 8,306.3220/T$$

derived from data points at 1200, 1700, and 2200 K from my spinel and ZnO tables and the 3rd ed JANAF Table for molten titania.

The final equation is

$$\log K = -0.14640 + 3,044.1203/T$$

for the reaction



References

Akaogi, M., Yusa, H., Ito E., Yagi, T., Suito, K., and Iiyama, J. T. (1990) The ZnSiO_3 clinopyroxene – ilmenite transition: Heat capacity, enthalpy of transition and phase equilibria. *Phys. Chem. Minerals* 17, 17-23.

Anthrop, D. F. and Searcy, A. W. (1964) Sublimation and thermodynamic properties of zinc oxide. *J. Phys. Chem.* 68, 2335-2342.

Björkman, B. (1986) An assessment of Cu, Ni and Zn silicate systems I. The binary systems $\text{CuO}_{0.5} - \text{SiO}_2$, $\text{NiO} - \text{SiO}_2$ and $\text{ZnO} - \text{SiO}_2$. *Scand. J. Met.* 15, 185-190.

Bonnicksen, K. R. (1955) High temperature heat contents of some titanates of aluminum, iron, and zinc. *J. Am. Chem. Soc.* 77, 2152-2154.

Bunting, E. N. (1930) Phase equilibria in the system $\text{SiO}_2 - \text{ZnO}$. *J. Am. Ceram. Soc.* 13, 5-10.

Clemmer, D. E., Dalleska, N. F., and Armentrout, P. B. (1991) Reaction of Zn^+ with NO_2 . The gas-phase thermochemistry of ZnO . *J. Chem. Phys.* 95, 7263-7268.

Dulin, F. H. and Rase, D. E. (1960) Phase equilibria in the system $\text{ZnO} - \text{TiO}_2$. *J. Am. Ceram. Soc.* 43, 125-131.

Egorov, A. M. and Smirnova, M. N. (1965) Mean specific heats of zinc and nickel orthosilicates at high temperatures. *Russ. J. Phys. Chem.* 39, 1137-1139.

Gilbert, I. G. F. and Kitchener, J. A. (1956) The free energy of formation of zinc aluminate. *Trans. Faraday Soc* 52, 3922-3924.

Hansson, R., Hayes, P. C., and Jak, E. (2004) Experimental study of phase equilibria in the Al-Fe-Zn-O system in air. *Met. Mat. Trans.* 35B, 633-642.

Jacob, K. T. (1976) Gibbs free energies of formation of ZnAl_2O_4 and ZnCr_2O_4 . *Thermochim. Acta* 15, 79-87.

Jacob, K. T. and Alcock, C. B. (1975) Evidence of residual entropy in the cubic spinel Zn_2TiO_4 . *High Temp High Press* 7, 433-439.

Jacob, K. T., Saji, V. S., and Reddy, S. N. S. (2007) Thermodynamic evidence for order – disorder transition in NiTiO_3 . *J. Chem. Thermo.* 39, 230-235.

Jak, E., Degterov, S. Wu, P., Hayes, P. C. and Pelton, A. D. (1997) Thermodynamic optimization of the systems $\text{PbO} - \text{SiO}_2$, $\text{PbO} - \text{ZnO}$ and $\text{PbO} - \text{ZnO} - \text{SiO}_2$. *Met. Mat. Trans.* 28B, 1011-1018.

King, E. G. (1951) Heats of formation of crystalline calcium orthosilicate, tricalcium silicate and zinc orthosilicate. *J. Am. Chem. Soc.* 73, 656-658.

King, E. G. (1955) Low-temperature heat capacities and entropies at 298.16 °K of some titanates of aluminum, calcium, lithium, and zinc. *J. Am. Chem. Soc.* 77, 2150-2152.

Kitchener, J. A. and Ignatowicz, S. (1951) The reduction equilibria of zinc oxide and zinc silicate with hydrogen. *Trans. Faraday Soc.* 47, 1278-1286.

Millard, R. L., Peterson, R. C., and Hunter, R. K. (1995) Study of the cubic to tetragonal transition in Mg_2TiO_4 and Zn_2TiO_4 spinels by ^{17}O MAS NMR and Rietveld refinement of X-ray diffraction data. *Am. Min.* 80, 885-896.

Navrotsky, A. (1986) Cation-distribution energetics and heats of mixing in $\text{MgFe}_2\text{O}_4 - \text{MgAl}_2\text{O}_4$, $\text{ZnFe}_2\text{O}_4 - \text{ZnAl}_2\text{O}_4$, and $\text{NiAl}_2\text{O}_4 - \text{ZnAl}_2\text{O}_4$ spinels: Study by high-temperature calorimetry. *Am. Min.* 71, 1160-1169.

Navrotsky, A. and Kleppa, O. J. (1968) Thermodynamics of formation of simple spinels. *J. Inorg. Nucl. Chem.* 30, 479-498.

Navrotsky, A. and Muan, A. (1970) Phase equilibria and thermodynamic properties of solid solutions in the systems ZnO-CoO-TiO_2 and ZnO-NiO-TiO_2 at 1050 °C. *J. Inorg. Nucl. Chem.* 32, 3471-3484.

Pedley, J. B. and Marshall, E. M. (1983) Thermochemical data for gaseous monoxides. *J. Phys. Chem. Ref. Data* 12, 967-1031.

Richet, P. and Bottinga, Y. (1986) Thermochemical properties of silicate glasses and liquids: A review. *Rev. Geophys.* 24, 1-25.

Tangeman, J. A., Phillips, B. L., Navrotsky, A., Weber, J. K. R., Hixson, A. D., and Key, T. S. (2001) Vitreous forsterite (Mg_2SiO_4): Synthesis, structure, and thermochemistry. *Geophys. Res. Lett.* 28, 2517-2520.

Watson, L. R., Thiem, T. L., Dressler, R. A., Salter, R. H., and Murad, E. (1993) High temperature mass spectrometric studies of the bond energies of gas-phase ZnO , NiO , and CuO . *J. Phys. Chem.* 97, 5577-5580.