

the mineral itself may be nonstoichiometric, or (d) the substitution of small amounts of a larger ion (eg. Se) may cause enough distortion of octahedral site symmetry for stabilization of larger amounts of the Cu^{2+} ion.

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THE AMERICAN MINERALOGIST, VOL. 55, MARCH-APRIL, 1970

CHEMICAL REACTIONS IN CRYSTALS: CORRECTIONS AND CLARIFICATION

JAMES B. THOMPSON, JR., *Department of Geological Sciences, Harvard University, Cambridge, Massachusetts 02138.*

CORRECTIONS

The following may be of some help to the baffled reader of my recent paper. Other, more obvious, misprints and lapses on my part have turned up, but the following includes those (at least the ones so far discovered) that appear most likely to cause trouble.

p. 345, equation (4): " Z_Q " not " Z_q "

p. 346, line following equation (5): "quantities" not "varieties"

p. 354, line following equation (30): " \bar{G}_1^o " not " \bar{G}^o "

p. 356, second line below caption: "univariant" not "invariant" [!]

p. 357, equation (40): " g_0 " not " $g0$ "

fourth line from bottom: T_{10} and T_{1m} [also true of T_{20} and T_{2m}]

p. 365, first two lines of text: The meaning would be clearer if the word "no" were entered before "symmetry," and the word "not" crossed out in the line below.

equations (47) and (49): " g_{ss} " should be " $2g_{ss}$ " [!]. This error proliferates below.

line below equation (50): insert "numerical" before "subscripts"

third line from bottom: " W_{M3} " should be " W_{M2} "

p. 366, equation (52):

$$\frac{W_M}{2RT} s \quad \text{should be} \quad \frac{W_M}{RT} s$$

discussion below (52): A second error involving a factor of 2 enters here. The mole of a 1:1 hypersthene would, according to the procedure established on pp. 344 and 349 and followed in Table A2 on p. 371, contain $\text{Fe}_2\text{Mg}_2\text{Si}_4\text{O}_{12}$. This discussion, however, and ensuing calculations, were based on a mole containing $\text{FeMgSi}_2\text{O}_6$. Conversion from the old mole to the new means that the quantity α (Thompson, 1967, Eq. 62), corresponding to q here, becomes 2 rather than 1. Critical unmixing at 25°C would then imply that W_M would be about 2.4 kcal, not 1.2 kcal. The effect of the combined errors on the calculated values of $\Delta\bar{S}^\circ$ and $\Delta\bar{H}^\circ$ at the base of the page is that they are all half what they should be for the indicated values of W_M . Taking 2 kcal as a more realistic maximum value for W_M the results would be: $(\bar{S}_{01}^\circ - \bar{S}_{01}^\circ) = -1.16$ cal/deg; and $(\bar{H}_{01}^\circ - \bar{H}_{01}^\circ) = -10.46$ kcal

p. 367, third line: "506°C" not "500°C", 513°C when $W_M = 1$ kcal is correct. The value when $W_M = 2$ kcal would be 521°C.

equation (53): " $2g_{ss}s$ " not " $g_{ss}s$ "

p. 368, equation (54):

$$\frac{\text{"artanh } s}{s} = -\frac{g_{ss}}{4} \quad \text{should be} \quad \frac{\text{"artanh } s}{s} = -\frac{g_{ss}}{2}$$

p. 369, second line below equation (57): " $s=0$ " should be " $r=0$ "

p. 370, lines below equation (A1): "terns" should be "terms"

" $(z_s - z_Q)$ " should be " $(Z_s - Z_Q)$ "

p. 372, third line below Table A3: "(9)" should be "(4)"

CLARIFICATION

The discussion beginning on p. 363 omits many steps. The following fills in some of the gaps and should answer some of the questions I have been asked since the appearance of my paper.

For a hypersthene of content: $(M2)_2(M1)_2(\text{Si}_4\text{O}_{12})$; we may write as a second-degree approximation:

$$\Gamma \equiv \frac{\bar{G}}{RT} = \left[\ln \frac{[(1 - r^2 - s^2)^2 - (2rs)^2]}{16} \right. \\ \left. + 2r \operatorname{artanh} \left(\frac{2r}{1 + r^2 - s^2} \right) + 2s \operatorname{artanh} \left(\frac{2s}{1 - r^2 + s^2} \right) \right] \\ + g_0 + g_r r + g_s s + g_{rr} r^2 + g_{rs} r s + g_{ss} s^2 \quad (1)$$

This may also be written in terms of site-occupancy fractions (N_{sq}) as follows, using (43), (44), (45), (50), and (51) of the original paper:

$$RT\Gamma = \bar{G} = 2RT[N_{11}\ln N_{11} + N_{21}\ln N_{21} + N_{12}\ln N_{12} + N_{22}\ln N_{22}] \\ + \bar{G}_{10}^{\circ}N_{11}N_{12} + \bar{G}_{10}^{\circ}N_{21}N_{22} + \bar{G}_{01}^{\circ}N_{21}N_{12} + \bar{G}_{01}^{\circ}N_{11}N_{22} \\ + W_{M1}N_{11}N_{21} + W_{M2}N_{12}N_{22} \quad (1a)$$

where the first subscripts, 1 and 2, refer to Mg and Fe, respectively, and the second subscripts refer to the M-sites. From (1) we obtain the following:

$$\Gamma_r \equiv \left(\frac{\partial\Gamma}{\partial r}\right)_s = 2 \operatorname{artanh}\left(\frac{2r}{1+r^2-s^2}\right) + g_r + 2g_{rr}r + g_{rs}s \quad (2)$$

$$\Gamma_s \equiv \left(\frac{\partial\Gamma}{\partial s}\right)_r = 2 \operatorname{artanh}\left(\frac{2s}{1-r^2+s^2}\right) + g_s + g_{rs}r + 2g_{ss}s \quad (3)$$

It is also useful to define Γ_m as the intercept, at the origin of r and s , of the tangent plane to the Γ -surface:

$$\Gamma_m \equiv \Gamma - r\Gamma_r - s\Gamma_s = \ln \frac{[(1-r^2-s^2)^2 - (2rs)^2]}{16} \\ + g_0 - (g_{rr}r^2 + g_{rs}rs + g_{ss}s^2) \quad (4)$$

At internal equilibrium $\Gamma_s=0$. We may therefore identify the chemical potentials of the components En , or $Mg_4Si_4O_{12}$, and Fs , or $Fe_4Si_4O_{12}$, in this simple example, as follows:

$$\frac{\mu_{En}}{RT} = \Gamma_m - \Gamma_r = \ln \frac{[(1-r^2-s^2)^2 - (2rs)^2]}{16} \\ - 2 \operatorname{artanh}\left(\frac{2r}{1+r^2-s^2}\right) + g_0 - g_r - 2g_{rr}r \\ - g_{rs}s - (g_{rr}r^2 + g_{rs}rs + g_{ss}s^2) \quad (5)$$

$$\frac{\mu_{Fs}}{RT} = \Gamma_m + \Gamma_r = \ln \frac{[(1-r^2-s^2)^2 - (2rs)^2]}{16} \\ + 2 \operatorname{artanh}\left(\frac{2r}{1+r^2-s^2}\right) + g_0 + g_r + 2g_{rr}r \\ + g_{rs}s - (g_{rr}r^2 + g_{rs}rs + g_{ss}s^2) \quad (6)$$

The exchange potential, $(\mu_{Fs} - \mu_{En})$, for heterogeneous Mg-Fe exchange equilibrium (as considered, for example, by Grover and Orville, 1969)

of an internally equilibrated hypersthene with another phase is also readily obtainable since $(\mu_{\text{Fs}} - \mu_{\text{En}}) = 2RT\Gamma_r$.

Relations (2) through (6) may be rewritten using site-occupancy fractions as follows:

$$2RT\Gamma_r = 2RT \ln \left(\frac{N_{22}N_{21}}{N_{12}N_{11}} \right) + (\bar{G}_{10}^\circ - \bar{G}_{10}^\circ) - W_{M1}(2N_{21} - 1) - \Delta G_x^\circ(N_{21} + N_{22} - 1) - W_{M2}(2N_{22} - 1) \quad (2a)$$

$$2RT\Gamma_s = 2RT \ln \left(\frac{N_{22}N_{11}}{N_{12}N_{21}} \right) + (\bar{G}_{01}^\circ - \bar{G}_{01}^\circ) - W_{M1}(2N_{11} - 1) + \Delta \bar{G}_x^\circ(N_{22} + N_{11} - 1) - W_{M2}(2N_{22} - 1) \quad (3a)$$

$$2RT\Gamma_m = 2RT \ln (N_{11}N_{21}N_{12}N_{22}) + (\bar{G}_{10}^\circ + \bar{G}_{10}^\circ) + W_{M1}(1 - 2N_{11}N_{21}) + \Delta \bar{G}_x^\circ(N_{11}N_{12} + N_{21}N_{22}) + W_{M2}(1 - 2N_{12}N_{22}) \quad (4a)$$

$$\mu_{\text{En}} = \bar{G}_{10}^\circ + 2RT \ln (N_{11}N_{12}) + [W_{M1}N_{21}^2 + \Delta \bar{G}_x^\circ N_{21}N_{22} + W_{M2}N_{22}^2] \quad (5a)$$

$$\mu_{\text{Fs}} = \bar{G}_{10}^\circ + 2RT \ln (N_{21}N_{22}) + [W_{M1}N_{11}^2 + \Delta \bar{G}_x^\circ N_{11}N_{12} + W_{M2}N_{12}^2] \quad (6a)$$

where $\Delta \bar{G}_x^\circ \equiv (\bar{G}_{01}^\circ + \bar{G}_{01}^\circ) - (\bar{G}_{10}^\circ + \bar{G}_{10}^\circ)$. Equations (5a) and (6a), allowing for the difference in the size of the mole, may be compared with equations (19) and (20) of Mueller (1962, p. 593). The bracketed terms in (5a) vanish if the second degree terms in (1) may be neglected ($0 = g_{rr} = g_{rs} = g_{ss}$), and it seems reasonable in this context to define "ideality" as independent on the condition that terms of higher than first degree in the expansion of \bar{G}^*/RT are not required. It should be observed, in hypersthene for example, that this is a more restrictive statement than that the energies for mixing on specific sites (W_M 's) vanish. Second degree terms may still appear in (1), (5a), and (6a) even if $W_{M1} = W_{M2} = 0$, owing to the possibility that $\Delta \bar{G}_x^\circ \neq 0$. A formula such as:

$$\mu_{\text{Fs}} = \bar{G}_{10}^\circ + 4RT \ln N_{\text{Fs}} \quad (7)$$

where $N_{\text{Fs}} = (N_{21} + N_{22})/2$ would not follow, however, from the definition of ideality suggested above without the *further* restriction that $s = 0$ (or $N_{21} = N_{22} = N_{\text{Fs}}$) or, in other words, that no ordering exists.

It should be emphasized that the chemical potentials of an internally

equilibrated hypersthene may be regarded as functions of r alone, at constant P and T , owing to the condition $\Gamma_s=0$. We can not eliminate s from (5) or (6) algebraically by using (3), however, because of the transcendental terms in each, although numerical solutions can readily be obtained using iterative procedures as outlined by Thompson and Waldbaum (1969).

My thanks to G. L. Hovis and D. R. Waldbaum for checking and double-checking the above.

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