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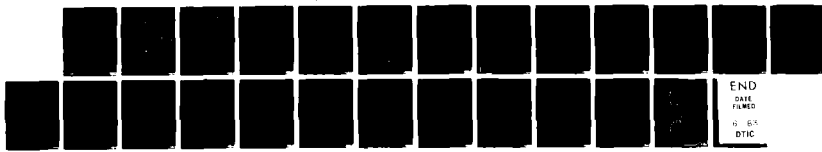
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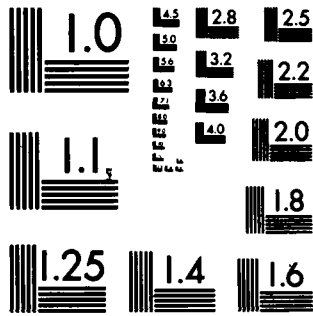
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A Working Model For the System Alumina-Magnesia

by
Richard A. Reinhardt
Naval Postgraduate School
for the
Research Department

MAY 1983

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NAVAL WEAPONS CENTER
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Naval Weapons Center

AN ACTIVITY OF THE NAVAL MATERIAL COMMAND

FOREWORD

This report documents the extension of the continuing research effort on internal blast at the Naval Weapons Center to include aluminized fuels in air. Work was performed during the period 1978-1982.

This effort was supported by the Naval Air Systems Command (NAVAIR) and was executed by the Naval Weapons Center under the Strike Warfare Weaponry Technology Block Program under AirTask A03W-03P2/008B/2F32-300-000 (appropriation 1721319.41AJ). This airtask provides for continued exploratory development in the air superiority and air-to-surface mission areas. Mr. H. B. Benefiel, AIR-350, was the cognizant NAVAIR Technology Administrator.

This report was reviewed for technical accuracy by K. J. Graham.

Approved by
E. B. ROYCE, *Head*
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5 May 1983

Under authority of
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(U) *A Working Model for the System Alumina-Magnesia*, by Richard A. Reinhardt, Naval Postgraduate School, China Lake, Calif., Naval Weapons Center, May 1983, 18 pp. (NWC TP 6-433, publication UNCLASSIFIED.)

(U) For treatment of internal explosions in the presence of both Mg and Al metals, it was necessary to devise a working model for the system magnesia-alumina. From the parameters of the model it was then possible to estimate equilibrium and internal-energy data for the various chemical species present in the oxide system, both in solid and liquid phases, for use in the blast computations.

(U) The solid phases, in agreement with published phase diagrams, consist of: (1) a magnesia phase, in which a small amount of spinel (magnesium aluminate) dissolves; (2) a spinel phase in which either magnesia or alumina is soluble to a considerable extent; and (3) a pure alumina phase. The solid phases were treated by the methods of the thermodynamics of non-ideal solutions. The melt was assumed to contain chemically reasonable ions, plus unionized MgO, and to behave as an ideal solution.

(U) The parameters of the model were adjusted to give the most satisfactory fit to the known phase diagram. It is emphasized that the model does not purport to be an actual explanation of the structure of the system.

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INTRODUCTION

PROBLEM

For solution of the internal explosion problem in systems containing both Mg and Al metals, there are needed representations for internal energies of the species present and for the chemical potentials of oxygen, aluminum, and magnesium as functions of temperature and composition. When aluminum oxide and magnesium oxide are both present in a condensed phase, the requirements of the equilibrium phase diagram must be met. This diagram shows a maximum in freezing point corresponding to the composition magnesium aluminate (MgAl_2O_4), or spinel, with an extensive solid-solution region on either side of the spinel composition, a restricted solid solution rich in magnesia, and substantially no solid solution in the vicinity of pure alumina.

REQUIREMENTS OF THE MODEL

The discontinuities in the solid solutions indicate considerable non-ideality in the solid phases (with activity coefficients very likely greater than unity). There is insufficient information to treat both liquid and solid phases as non-ideal. Hence the liquid solutions will be assumed to be ideal.

DATA AVAILABLE

JANAF:¹ internal energies (computed from enthalpies) and equilibrium constants of formation for MgO (liquid and solid) and MgAl_2O_4 (solid only). Melting points agree well with recent phase diagrams (*vid. inf.*).

Phase equilibrium data:^{2,3} the data for MgO-spinel appear more reliable than those for Al_2O_3 -spinel. Several regions in the resulting diagram appear rather uncertain: the liquidus

¹National Bureau of Standards. *JANAF Thermochemical Tables*, by D. R. Stull and H. Prophet, 2nd ed. Washington, D. C., NBS, June 1971.

²A. M. Alper, R. N. McNally, P. H. Ribbe, and R. C. Doman. "The System MgO-MgAl₂O₄," in *J. Amer. Ceram. Soc.*, Vol. 45 (June 1962), p. 265.

³D. Viechnicki, F. Schmidt, and J. W. McCauley. "Liquidus-Solidus Determinations in the System MgAl₂O₄-Al₂O₃," in *J. Amer. Ceram. Soc.*, Vol. 57, No. 1 (January 1974), p. 47.

for Al_2O_3 in spinel (which must be surmised, except for a few scattered points near the eutectic), the solidus for MgO in spinel (a rather short region in which no experimental points are shown), and the lower bounds for the solid solutions, which are merely estimated to be at about 1500°C (1800 K).

NOTATION

The composition of the liquid phase will be designated Y, giving the mole-fraction of MgO on the basis of MgO and Al_2O_3 as the components. The composition of solid phases will usually be designated by X_i , which is the mole-fraction of component i on the basis of MgO and spinel or Al_2O_3 and spinel as the components. For some purposes it is convenient to consider MgO and Al_2O_3 as components of the solid. The symbol Z will be used for the mole-fraction in MgO on this basis. Note that $Z = X_{\text{Sp}}/(1 + X_{\text{Sp}})$ when the components are considered to be spinel and Al_2O_3 , and $Z = 1/(1 + X_{\text{Sp}})$ when components are spinel and MgO.

Mole-fractions of individual species in the liquid phase will be indicated by writing the formula of the substance. Since the solutions are considered ideal, the activity of each species is treated as equal to its mole-fraction in the liquid. The standard state for each is the pure liquid, which is of course hypothetical for the ionic species.

Activities for MgO, spinel, or Al_2O_3 in the solid phases are written a_j . The standard state for each is the pure solid.

Melting-point equilibria are presented as equilibrium constants. For MgO, S_{Ma} is defined as the ratio of the K_f values for the liquid divided by that for the solid, and would be the ratio of the activities of MgO in the two phases if MgO is considered undissociated in the liquid. For Al_2O_3 , S_{Ao} is used for the similar quantity. If complete dissociation is assumed ($\text{AB} \rightarrow \text{A} + \text{B}$), then $S_{\text{AB}} = K_{\text{liq}}/K_{\text{sol}} = \text{moles (A)}/(1 + \text{moles (A)})$ which can be shown equal to $\text{A}/(1 - \text{A})$, in mole-fractions, or $\text{A} = \text{S}/(1 + \text{S})$. But since $\text{A} = \text{B}$, the "solubility product," $K_{\text{AB}} = [\text{S}/(1 + \text{S})]^2$.

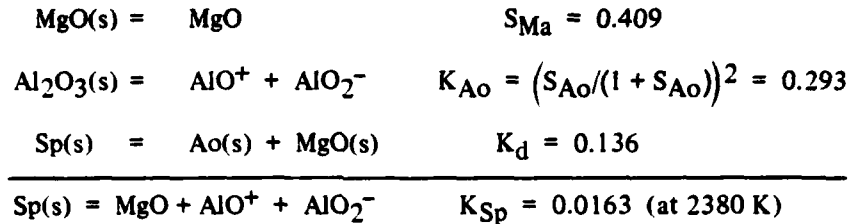
The equilibrium constant for the dissociation of spinel in the solid will be denoted $K_d = a_{\text{MgO}} \cdot a_{\text{Ao}}/a_{\text{Sp}}$. Here and elsewhere are used the abbreviations Ao for Al_2O_3 and Sp for spinel. The symbol used for the mole-fraction of ions will often lack charge.

THE MODEL USED

Species assumed present in the liquid are MgO, Mg^{2+} , AlO^+ , and AlO_2^- . Thus MgO dissolves without dissociation, spinel dissolves partly as $\text{Mg}^{2+} + 2\text{AlO}_2^-$ and Al_2O_3 as $\text{AlO}^+ + \text{AlO}_2^-$; but these last two are modified by the necessity to consider the "neutralization" equilibrium, $\text{MgO} + \text{AlO}^+ = \text{Mg}^{2+} + \text{AlO}_2^-$.

PURE SPINEL AT ITS MELTING POINT, 2380 K

Consider the reactions, each with its respective equilibrium constant:



By computing K_{Sp} at several other temperatures it is found that the temperature coefficient, expressed as $d(\ln K_{\text{Sp}})/d(1/T)$ is -24.8 K .

In general, three equations must be satisfied:

$$\text{Mole-fraction: } \text{MgO} + \text{Mg} + \text{AlO} + \text{AlO}_2 = 1 \quad (1)$$

$$\text{Charge: } \text{AlO}_2 = \text{AlO} + 2\text{Mg} \quad (2)$$

$$\text{Composition: } Y = (\text{Mg} + \text{MgO}) / (\text{Mg} + \text{MgO} + 1/2(\text{AlO} + \text{AlO}_2)) \quad (3)$$

These three equations combined with the expression for K_{Sp} , lead to the cubic

$$\text{AlO} \cdot \text{AlO} \cdot (2/3 - \text{AlO}) = 0.0163, \text{ from which, at 2380 K,}$$

$$\text{AlO} = \text{MgO} = 0.184$$

$$\text{Mg} = 0.150$$

$$\text{AlO}_2 = 0.483$$

And thus can be computed the neutralization constant

$$K_{\text{n}} = (\text{Mg} \cdot \text{AlO}_2) / (\text{MgO} \cdot \text{AlO}) = 2.140 \text{ at 2380 K}$$

TENTATIVE RESULTS

Approximate calculations were performed, using experimental Y values, on the basis of an assumed temperature coefficient of K_{η} . These calculations showed that in the MgO solid solution (minimum $X_{\text{MgO}} = 0.922$) it may be reasonably assumed that Raoult's law applies to the solvent, MgO, and Henry's law to the solute spinel. Thus $a_{\text{MgO}} = X_{\text{MgO}}$ and $a_{\text{Sp}} = k \cdot X_{\text{Sp}}$, where k is the Henry's law constant, equal to a constant activity coefficient, to be determined.

In the solutions of MgO in spinel, these tentative computations show that

$$\ln a_{\text{MgO}} = a + br^{1/2} \quad (4)$$

where

$$r = X_{\text{MgO}}/X_{\text{Sp}}$$

This curious behavior results from the choice of components used. The activity of MgO does not fall to zero in pure spinel because of the dissociation. As a result, Henry's law will not hold for MgO even in the limit.

The calculations also give $a_{\text{MgO}} = 0.449$ and $a_{\text{Ao}} = 0.303$ in pure spinel at its melting point, 2380 K. It will be assumed that the ratio $a_{\text{MgO}}/a_{\text{Ao}}$ in pure spinel is independent of temperature. Now the dissociation constant, $K_d = a_{\text{MgO}} \cdot a_{\text{Ao}}/a_{\text{Sp}}$, and for pure spinel $a_{\text{Sp}} = 1$. Thus it may be said that

$$a_{\text{MgO}} = (1.84 \cdot K_d)^{1/2} \text{ and } a_{\text{Ao}} = a_{\text{MgO}}/1.484 \quad (5)$$

in pure spinel at any temperature.

For alumina in spinel, the tentative results indicate that

$$\ln a_{\text{Ao}} = a' + b' \cdot X_{\text{Ao}} \quad (6)$$

APPLICATION OF THE GIBBS-DUHEM EQUATION

For any binary system⁴

$$X_1 d \ln a_1 = -X_2 d \ln a_2 \quad (7)$$

When applied to the solid solutions of MgO in spinel, where

$$\ln a_{\text{MgO}} = a + br^{1/2} \quad (4)$$

⁴G. N. Lewis and M. Randall. *Thermodynamics*, 2nd ed., revised by K. S. Pitzer and L. Brewer, McGraw-Hill, New York, N.Y., 1961, Chapter 20.

it follows that

$$\ln a_{Sp} = -b/3 r^{3/2} \quad (8)$$

At 2270 K (the MgO-Sp eutectic temperature), a_{MgO} in pure spinel equals 0.440 (from Equation 5) thus $a = -0.821$. The MgO solid solution at the eutectic temperature has the composition $X_{MgO} = 0.922$, so that (in view of the assumption of Raoult's law in this solution) $a_{MgO} = 0.922$ in the eutectic at 2270 K. The value of r is obtained from the composition of the spinel solid solution at the eutectic

$$X_{MgO} = 0.350$$

From this, b is computed to be 1.008 at 2270 K.

For the Ao-Sp solid solutions it was found that

$$\ln a_{Ao} = a' + b' \cdot X_{Ao} \quad (6)$$

from which application of the Gibbs-Duhem equation (Equation 7) shows

$$\ln a_{Sp} = b' (X_{Ao} + \ln X_{Sp}) \quad (9)$$

At 2250 K, the temperature of the Ao-Sp eutectic (Equation 5) gives $a_{Ao} = 0.295$ in pure spinel, so that $a' = -1.221$. The spinel solid solution at the eutectic has $X_{Ao} = 0.809$; the activity of alumina at the eutectic is set equal to unity since there is essentially no solubility of spinel in alumina. As a consequence, $b' = 1.509$ at 2250 K. Using this, a_{Sp} at the eutectic comes to 0.279, which compares favorably with the tentative value of 0.258 (computed from Y).

EVALUATION OF ENTHALPY OF NEUTRALIZATION

Given a_{MgO} and a_{Sp} , Y and K_n can be found as follows

$$MgO = a_{MgO} \cdot S_{Ma}$$

$$MgO \cdot AlO \cdot AlO_2 = a_{Sp} \cdot K_{Sp}$$

Hence

$$AlO \cdot AlO_2 = a_{Sp} \cdot K_{Sp} / (a_{MgO} \cdot S_{Ma}) = K'$$

When applied to the MgO-spinel eutectic at 2270 K,

$$K' = 0.876 \cdot 0.0098 / (0.922 \cdot 0.341) = 0.0274$$

Combined with Equations 1 and 2, the foregoing permits solution for all four components in this system:

$$\text{AlO}_2^- = 0.4361$$

$$\text{AlO}^+ = 0.028$$

$$\text{Mg}^{2+} = 0.1867$$

$$\text{MgO} = 0.3144$$

Thus

$$K_n = 0.1867 \times 0.4361 / (0.3144 \times 0.0628) = 4.124 \text{ at } 2270 \text{ K.}$$

When this result is combined with the K_n previously found at 2380 K (2.140), the energy change for the neutralization reaction, ΔH_n , is found to be -268 kJ/mole.

Substitution into Equation 3 yields $Y = 0.668$ for the eutectic solution, comparing favorably with the experimental $Y = 0.677$.

BOUNDARIES OF THE SOLID SOLUTIONS

MgO Solid Solutions

The solidus curve (the point of first melting) is given by Alper, et al.² An empirical representation is

$$Z = 0.922 + 0.000153 (T - 2270) - 7.1 \times 10^{-8} (T - 2270)^2 \quad (10)$$

$$(2270 < T < 3100)$$

The isothermal limits of the solid solution (the boundary separating the one-solid and two-solid regions) is not known. A linear representation has been assumed with the known eutectic point as the upper limit and assuming 1800 K as the lower limit, so that

$$X_{Sp} = k_4 t \quad (11)$$

where

$$t = T - 1800$$

$$k_4 = 0.00016$$

Spinel Solid Solution, MgO Side

The data of Alper, et al. allow only an estimation of the solidus;² nonetheless, the termini (melting point of pure spinel and the triple point) are given. A quadratic form of the same sort as used for the other two solidus curves was assumed

$$Z = 0.608 - 0.00155 (T - 2270) + 5.1 \times 10^{-6} (T - 2270)^2 \quad (12)$$

$$(2270 < T < 2380)$$

For the limiting solubility of the solid solution, again a linear relation is assumed

$$X_{Sp} = 1 - k_1 t \quad (13)$$

where

$$t = T - 1800$$

$$k_1 = 0.000745$$

Spinel Solid Solution, Alumina Side

Data for the solidus are given by Viechnicki, et al.³ A reasonable fit is given by

$$Z = 0.150 + 0.00512(T - 2250) - 1.86 \times 10^{-5} (T - 2250)^2 \quad (14)$$

$$(2250 < T < 2380)$$

For the limiting solubility of the solid solution the assumed relation is

$$X_{Sp} = 1 - k_7 t \quad (15)$$

where

$$t = T - 1800$$

$$k_7 = 0.00183$$

ACTIVITIES IN THE SOLID SOLUTIONS**Z Greater Than 0.5**

In the spinel-MgO solid solution, as discussed previously, the activities of the components are represented by

$$\ln a(\text{MgO}) = a + br^{1/2} \quad (4)$$

$$\ln a_{Sp} = -b/3 r^{3/2} \quad (8)$$

where

$$r = X_{\text{MgO}}/X_{\text{Sp}}$$

The parameter a is found at each temperature, as discussed previously

$$a = \ln a_{\text{MgO}}'$$

where a_{MgO}' is the activity in pure spinel and is given by Equation 4 as

$$(1.48 \cdot K_d)^{1/2}$$

A satisfactory empirical representation is given by

$$a = -k_2 + k_3/T \quad (16)$$

where

$$\begin{aligned} k_2 &= 0.2252 \\ k_3 &= -1348 \end{aligned}$$

Next, b is found by using the following concepts. In the region of two solid phases, a_{MgO} and a_{Sp} are the same for the two phases. Raoult's law is assumed for MgO in the MgO solid solution, so that along the solubility limit of that solid solution, $a_{\text{MgO}} = X(\text{MgO in MgO}) = 1 - k_4 t$, from Equation 11. This value applies also to the spinel solid solution in equilibrium, for which $r = X_{\text{MgO}}(\text{in Sp})/X_{\text{Sp}}(\text{in Sp})$; and from Equation 13 it follows that

$$r = 1/k_1 t - 1 \quad (17)$$

Substituting the values for a_{MgO} , a , and r from Equations 4, 16, and 17, it is found that

$$b = (k_1 t / (1 - k_1 t))^{1/2} (k_2 - k_3/T + \ln(1 - k_4 t)) \quad (18)$$

where

$$\begin{aligned} k_1 &= 0.000745 \\ k_2 &= 0.2252 \\ k_3 &= -1348 \\ k_4 &= 0.00016 \\ t &= T - 1800. \end{aligned}$$

Values at several temperatures are given in Table 1. The values of a and b so found are then used to compute a_{Sp} , from which is found $\gamma_{\text{Sp}} = a_{\text{Sp}}/X(\text{Sp in MgO})$. The results of the calculation, when extended above 2250 K, are in fair agreement with those computed by the use of Equations 1 and 2 combined with the values of S_{Ma} and X_{MgO} along the liquidus: disagreement as large as 25%, however, is observed in places. γ_{Sp} is constant at any temperature throughout the MgO solid solution (a consequence of the assumed conformity to Henry's law for the solute, spinel).

TABLE 1. Constants Used in the Calculation of the Phase Diagram (MgO-Spinel).

Temperature, K	a	X _{MgO} (MgO)	X _{Sp} (in Sp)	b	a _{Sp}	γ _{Sp}
1900	-0.936	0.984	0.926	3.25	0.976	52.5
2000	-0.898	0.968	0.851	2.07	0.951	30.0
2100	-0.865	0.953	0.777	1.52	0.925	19.8
2200	-0.839	0.938	0.702	1.19	0.896	14.4
2270	-0.821	0.922	0.650	1.01	0.876	11.2

Alumina-Spinel Solid Solutions

It was previously pointed out that the activities here could be represented by

$$\ln a_{\text{Ao}} = a' + b' \cdot X_{\text{Ao}} \quad (6)$$

$$\ln a_{\text{Sp}} = b' (X_{\text{Ao}} + \ln X_{\text{Sp}}) \quad (9)$$

Using a_{Ao}' for the activity of alumina in pure spinel, by analogy with the treatment for MgO, it may be written that

$$a' = \ln a_{\text{Ao}}' = \ln(a_{\text{MgO}}'/1.484)$$

at each temperature. In the two-solid region the solid solution is in equilibrium with pure alumina, or $a_{\text{Ao}} = 1$. Thus, for X_{Sp} along the solubility boundary b' can be computed, again much as for the MgO case. Some results are given in Table 2.

RECONSTRUCTION OF THE PHASE DIAGRAM

Based on the foregoing, it has been possible to reconstruct the temperature-composition diagram for solid-liquid equilibria in the system MgO-Al₂O₃. The solidus curves, Z as a function of T, were constructed according to the discussion in the section entitled "Boundaries of the Solid Solutions" using Equations 10, 12, and 14. Activities of Ao and MgO were computed from the methods described in the section entitled "Activities in the Solid Solutions." These values, combined with the stoichiometric relations (1), (2), and (3) and the value of K_n permit computation of Y, the composition of liquid solution in equilibrium with solid at the chosen temperature.

TABLE 2. Constants Used in the Calculation of the Phase Diagram (Alumina-Spinel).

Temperature, K	a'	X _{Sp}	b'	a _{Sp}	γ _{Sp}
1900	-1.331	0.817	7.273	0.870	1.06
2000	-1.293	0.634	3.533	0.728	1.15
2100	-1.260	0.451	2.295	0.567	1.26
2200	-1.234	0.268	1.685	0.373	1.39
2250	-1.221	0.176	1.477	0.260	1.47

Figure 1 shows the results of these calculations. Squares represent the data reported in the literature;^{2,3} the solid curves pass through the computed points. The figure also indicates the solid-solid boundaries. The agreement with experiment is considered excellent for MgO solutions and considered good for spinel solutions (especially considering the uncertainties in reported data). The most serious disagreement is seen in the region of the Ao-Sp eutectic, where the error is about 0.05 in mole-fraction.

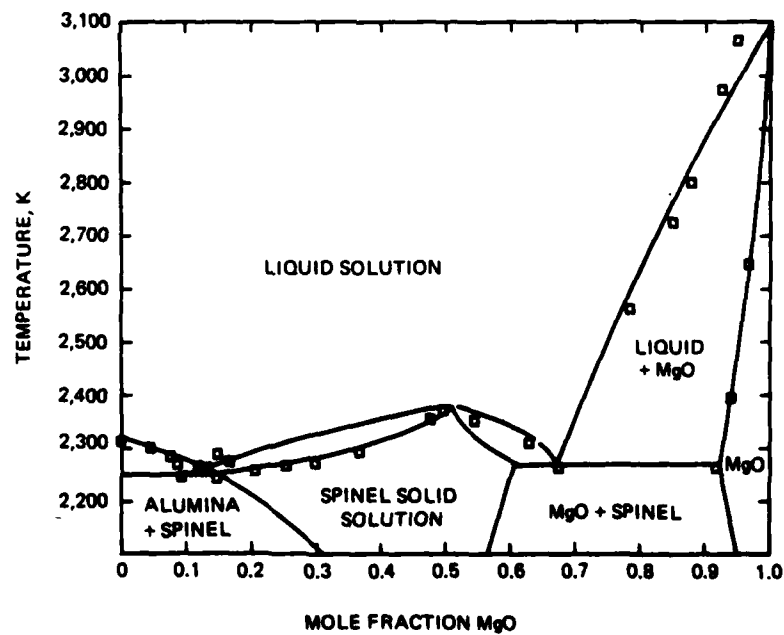


FIGURE 1. Phase Diagram for the System MgO-Al₂O₃.

ENTHALPIES IN THE SOLID SOLUTIONS

THEORY

The treatment here is basically the same as that of Lewis and Randall.⁴ The relative partial molal enthalpy of component i is defined by

$$\bar{L}_i = \bar{H}_i - \bar{H}_i^0 \quad (19)$$

where \bar{H}_i is the partial molal enthalpy in the solution and \bar{H}_i^0 that in the reference state, which, for all our cases is the pure component. Thus, for n_i moles, the contribution to the enthalpy in the solution is

$$\bar{H}_i = n_i \bar{H}_i = n_i (\bar{L}_i + \bar{H}_i^0) \quad (20)$$

For an ideal solution each \bar{L}_i is zero.

It is also shown in the reference cited as footnote 4 that

$$\partial \ln \gamma_i / \partial T = \bar{L}_i / RT^2 \quad (21)$$

or the equivalent

$$\partial \ln \gamma_i / \partial (1/T) = -\bar{L}_i / R$$

MgO SOLID SOLUTIONS

These solutions are assumed "dilute" in the sense that Raoult's law is considered to apply to MgO and Henry's law to spinel. As a result, the activity coefficient of MgO is always unity, and thus $\bar{L}_{\text{MgO}}(\text{in MgO})$ is zero.

If $\log \gamma_{\text{Sp}}$ is plotted against $1/T$, using the values from Table 1, a somewhat S-shaped curve is obtained. It can be safely presumed that data at the lower temperatures are unreliable due to the arbitrary nature of Equation 11 used for the solid solution boundary. If these lower points are disregarded, as well as those at the highest temperatures (where again there is appreciable nonlinearity), a slope is found for $d \ln \gamma_i / d(1/T)$ of 13800 K, so that $\bar{L}_{\text{Sp}}(\text{in MgO}) = -115$ kJ/mole (from Equation 21). In principle, the temperature dependence at each point could have been used, but the uncertainties in the data do not warrant this refinement.

MgO IN SPINEL SOLID SOLUTIONS

From Equations 4 and 8 and the definition of activity coefficient

$$\ln \gamma_{\text{MgO}} = a + br^{1/2} - \ln X_{\text{MgO}}$$

$$\ln \gamma_{\text{Sp}} = -b/3 r^{3/2} - \ln X_{\text{Sp}}$$

The derivatives at constant composition become

$$\frac{d \ln \gamma_{\text{MgO}}}{d(1/T)} = \frac{da}{d(1/T)} + \sqrt{r} \frac{db}{d(1/T)} \quad (22)$$

$$\frac{d \ln \gamma_{\text{Sp}}}{d(1/T)} = \frac{-r^{3/2}}{3} \frac{db}{d(1/T)} \quad (23)$$

Although an exact representation for the derivatives called for by Equations 22 and 23 is possible, it is more realistic to use a simple empirical expression. It is found that (to within 2%)

$$b = b_1 + b_2/T \quad (24)$$

where

$$b_1 = -7.375$$

$$b_2 = 18.8 \times 10^3 \text{ K.}$$

In addition, examination of Table 1 shows that da/dT is negligible compared with db/dT . Thus we write, using Equations 21 through 24

$$\bar{L}_{\text{MgO}}(\text{in Sp}) = -Rr^{1/2} b_2 \quad (25)$$

$$\bar{L}_{\text{Sp}}(\text{in Sp}) = -R/3 r^{3/2} b_2 \quad (26)$$

SPINEL-ALUMINA SOLID SOLUTIONS

By application of Equations 6 and 9, we obtain the analogs of Equations 22 and 23.

$$\frac{d \ln a_{Ao}}{d(1/T)} = X_{Ao} \frac{db'}{d(1/T)} + \frac{da'}{d(1/T)} \quad (27)$$

$$\frac{d \ln a_{Sp}}{d(1/T)} = (X_{Ao} + \ln X_{Sp}) \frac{db'}{d(1/T)} \quad (28)$$

Again the variation in a' may be neglected. The empirical relation

$$b' = b_3 + b_4/T \quad (29)$$

where

$$b_3 = -15.1$$

$$b_4 = 37.0 \times 10^3 \text{ K}$$

represent the data to about 10%. As a result we may write

$$\bar{L}_{Ao}(\text{in Sp}) = -R b_4 X_{Ao} \quad (30)$$

$$\bar{L}_{Sp}(\text{in Ao}) = -R(X_{Ao} + \ln X_{Sp})b_4 \quad (31)$$

SUMMARY

The enthalpies in the solid phases may now be tabulated with numerical values. The symbol H^* is used in Table 3 for the enthalpy of the pure phase.

TABLE 3. Molar Enthalpies for the Solid Phases Present in the System MgO-Al₂O₃.

Component	Phase	Molar enthalpy, kJ/mole
MgO	MgO	H^*_{MgO}
Spinel	MgO	$H^*_{Sp} - 115$
MgO	MgO-Sp	$H^*_{MgO} - 156 r^{1/2}$
Spinel	MgO-Sp	$H^*_{Sp} - 52 r^{3/2}$
Alumina	Ao-Sp	$H^*_{Ao} - 307 X_{Ao}$
Spinel	Ao-Sp	$H^*_{Sp} - 307 X_{Ao} - 37 \ln(1 - X_{Ao})$

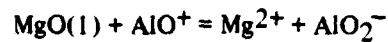
ENTHALPIES IN THE LIQUID SOLUTION

The JANAF tables give enthalpies for fused MgO and fused Al₂O₃, denoted in the following as J_{MgO} and J_{AlO}, respectively.¹ From the model presented it can be said that

$$H_{MgO} = J_{MgO} \quad (32)$$

$$H_{AlO} + H_{AlO_2} = J_{AlO} \quad (33)$$

In addition, the enthalpy change of the "neutralization" reaction,



was given as $\Delta H_n = -268$ kJ, so that

$$H_{Mg} + H_{AlO_2} - H_{MgO} - H_{AlO} = -268 \text{ kJ} \quad (34)$$

In an ionic medium, any one of the ionic enthalpies may be chosen arbitrarily (as is done with H⁺ in aqueous systems). It is thus convenient to set $H_{AlO_2} = 0$ at all temperatures. The remaining enthalpies become

$$H_{MgO} = J_{MgO}$$

$$H_{AlO} = J_{AlO}$$

$$H_{Mg} = J_{MgO} + J_{AlO} - 268 \text{ kJ}$$

APPLICATION

This model has been devised to provide an estimate of the thermodynamic parameters of the components of the MgO-Al₂O₃ system. It should not be construed as an attempt to represent the actual thermodynamic behavior of the system, but only a simplified one which is consistent with the melting-point diagram.

Appendix A

REJECTED MODELS

A large number of possible models for the system were examined and rejected on the basis of poor fit. Two examples are given, indicating the unsatisfactory features in some detail; there follows a listing of other models with a brief reason for the rejection. Each case is identified by the species assumed present in the liquid.

1. MgO, Ao, Sp

For the equilibrium

$$\begin{aligned} \text{Sp(s)} &= \text{MgO(1)} + \text{Ao(1)}, K = \text{MgO} \cdot \text{Ao} = S_{\text{Ma}} \cdot S_{\text{Ao}} \\ &= 0.136 \cdot 0.409 = 0.0656 \text{ at } 2380 \text{ K} \end{aligned}$$

(melting point of pure spinel). In this solution $\text{MgO} = \text{Ao} = 0.0656^{1/2} = 0.26$; and thus

$$S_{\text{p}} = 1 - 2(0.26) = 0.47$$

The dissociation constant of spinel in the solution phase,

$$D = \text{MgO} \cdot \text{Ao}/S_{\text{p}} = 0.26 \cdot 0.26/0.47 = 0.15$$

This relation is combined with the material balance and the expression for Y, which here becomes $(\text{MgO} + \text{Sp})/(1 + \text{Sp})$. These three equations, for any given value of Y, permit solution of the three mole-fractions.

For example, in saturated MgO at 2300 K, $Y = 0.689$, from which it can be computed that $\text{MgO} = 0.587$. The solid solution in equilibrium at 2300 K has $X_{\text{MgO}} = 0.930$; S_{Ma} at this temperature is 0.339. Thus is computed $a_{\text{MgO}} = \text{MgO}/(X_{\text{MgO}} \cdot S_{\text{Ma}}) = 0.587/(0.93 \cdot 0.339) = 1.86$. Since it is impossible for the chemical potential of a component in a solution to exceed that of the pure component, the model may be rejected at once. It may be remarked that the result given here is typical of all the points for which the calculation was tried.

2. Mg⁺⁺, O⁻⁻, AlO⁺, AlO₂⁻

The solubility equilibria applicable to pure spinel at 2380 K are

$$\text{MgO(s)} = \text{Mg}^{++} + \text{O}^{--}, K_{\text{MgO}} = \left[\frac{S_{\text{Ma}}}{1 + S_{\text{Ma}}} \right]^2 = 0.0842$$

$$\text{Ao(s)} = \text{AlO}^+ + \text{AlO}_2^-, K_{\text{Ao}} = \left[\frac{S_{\text{Ao}}}{1 + S_{\text{Ao}}} \right]^2 = 0.293$$

When these are combined with $K_d = 0.136$, one finds for the solution of spinel

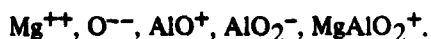
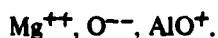
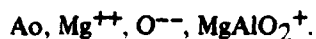
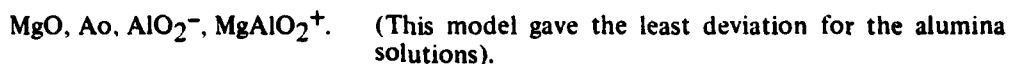
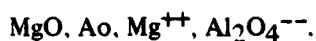
$$\text{Sp(s)} = \text{Mg}^{++} + \text{O}^{--} + \text{AlO}^+ + \text{AlO}_2^-, K_{\text{Sp}} = K_{\text{MgO}} \cdot K_{\text{Ao}} \cdot K_d = 0.0036$$

This equation is then combined with the material balance ($\text{Mg}^{++} + \text{O}^{--} + \text{AlO}^+ + \text{AlO}_2^- = 1$), the charge balance ($2\text{Mg}^{++} + \text{AlO}^+ = 2\text{O}^{--} + \text{AlO}_2^-$), and the stoichiometric condition

$$Y = 0.5 = \frac{\text{Mg}^{++}}{[\text{Mg}^{++} + 1/2(\text{AlO}^+ + \text{AlO}_2^-)]}$$

There results a quartic equation in O^{--} , for which the smallest root is 0.391, leading to negative values for both Mg^{++} and AlO_2^- .

3. The following models all resulted in a_{MgO} in the range 1.2 to as much as 1.8 for saturated MgO at the lower temperatures

4. Mg⁺⁺, O⁻⁻, AlO⁺, MgAlO₂⁺

For this model no solution exists that satisfies the equilibrium and stoichiometric requirements in pure spinel.

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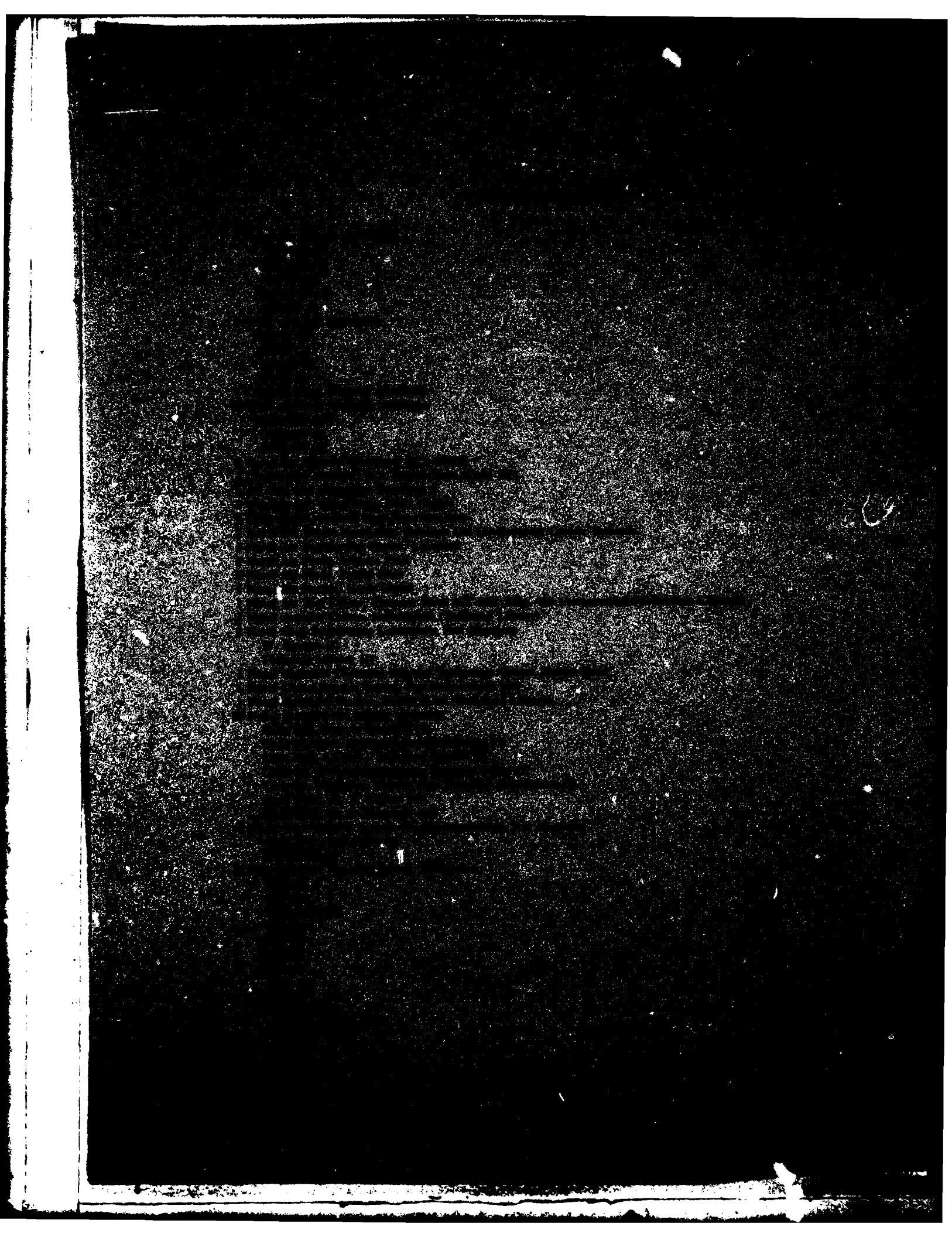
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