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THE OXIDATION OF ALMANDINE AND IRON CORDIERITE

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ABSTRACT

Solid solutions of the two end members magnetite and hercynite are common oxidation products of aluminous iron silicates. Activity coefficients for both components may be derived from the solvus in the system Fe_3O_4-$FeAl_2O_4$. It is then possible to calculate oxidation equilibria involving almandine, iron cordierite, sillimanite, and pure magnetite from experimental data.

INTRODUCTION

At high temperatures, the oxidation products of aluminous silicates commonly include solid solutions of magnetite and hercynite. The existence of a solvus in the system Fe_3O_4-$FeAl_2O_4$ indicates that these solutions are non-ideal. Consequently, thermodynamic calculations in the system SiO_2-Al_2O_3-FeO-O should involve activity coefficients. These may be derived from the solvus. It then becomes possible to calculate the standard free energy changes of several experimentally determined reactions and by linear combinations obtain standard free energy changes of other reactions of interest. This information allows the calculation of phase-relations in the system SiO_2-Al_2O_3-FeO-O. Essentially this procedure represents an extrapolation of relatively high temperatures experimental data to lower temperatures. This is of particular significance because, in the presence of quartz, the only stable oxide phase at lower temperatures is nearly pure magnetite. Thus it becomes possible to calculate oxidation reactions at metamorphic conditions involving almandine, iron cordierite, sillimanite, and pure magnetite.

DERIVATION OF ACTIVITY COEFFICIENTS

The unit cell of the spinel structure contains 8 cations in 4-fold coordination (*A* positions) and 16 cations in 6-fold coordination (*B* positions). In most spinels, the structure conforms closely to either one of two types of cation distribution :

normal : $8R^{++}$ in A, $16R^{+++}$ in B
inverse : $8R^{+++}$ in A, $8R^{++}$ and $8R^{+++}$ in B

The magnetite structure is close to inverse, whereas in hercynite the cation distribution is essentially normal (Navrotsky & Kleppa 1967). Accordingly, their formulas may be written as $Fe^{+++}(Fe^{++}Fe^{+++})O_4$ and $Fe^{++}(Al_2)O_4$. The regular variation of the unit cell dimension with composition (Turnock & Eugster 1962) suggests that there is a gradual change of structure in magnetite-hercynite solid solutions. In solutions, mixing of atoms in the two lattice sites would be expected rather than mixing of Fe_3O_4 and $FeAl_2O_4$ formula units. As an approximation, magnetite and hercynite will be regarded as a binary solution of iron and aluminum atoms in the *B* positions, *i.e.* $Fe_{0.5}FeO_2$ and $Fe_{0.5}AlO_2$ will be treated as the two components. Since such a model neglects mixing in the *A* positions and varying ratios of Fe^{++}/Fe^{+++} in the *B* positions,

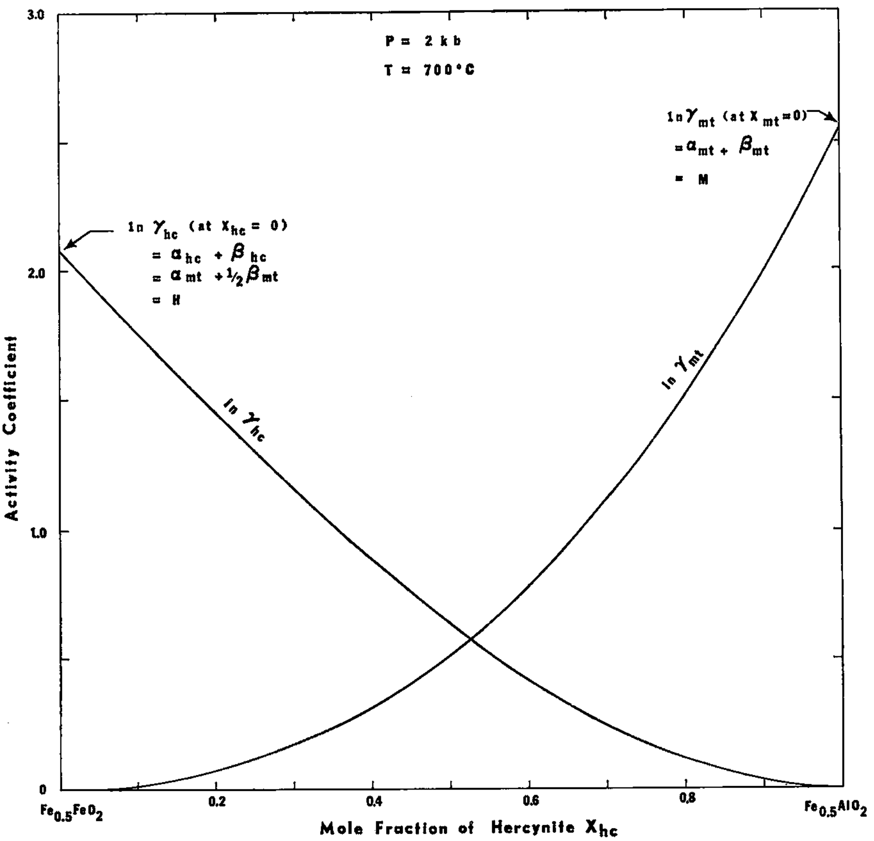

FIG. 1. Variation of activity coefficients with composition.

large deviations from ideality are not surprising. These will be accounted for by activity coefficients derived from the solvus.

The activity of a component in solution may be defined by the relationship $\mu = \mu^* + RT \ln a$, where μ is the chemical potential of the component in solution at stated pressure and temperature, μ^* is the chemical potential of the pure substance in a specified structural state and at the same pressure and temperature, and a is the activity. It is convenient to relate the activity to the mole fraction X by means of the activity coefficient γ, such that $a = \gamma X$.

At constant pressure and temperature, activity coefficients are functions of composition. In a binary solution, a fairly simple relationship is commonly observed, e.g. as shown in Figure 1. It is convenient to express this function empirically as a power series in $(1 - X)$ where X is the mole fraction of the component in question, as suggested by Margules (1895). Designating the component $Fe_{0.5}FeO_2$ as mt and the component $Fe_{0.5}AlO_2$ as hc, it is possible to write

$$\ln\gamma_{mt} = \lambda_{mt}(1 - X_{mt}) + \alpha_{mt}(1 - X_{mt})^2 + \beta_{mt}(1 - X_{mt})^3 + \dots$$

$$\ln\gamma_{hc} = \lambda_{hc}(1 - X_{hc}) + \alpha_{hc}(1 - X_{hc})^2 + \beta_{hc}(1 - X_{hc})^3 + \dots$$

This empirical relationship is consistent with two limiting laws; at $X = 1$, $\ln\gamma = 0$ (Raoult's Law) and at $X = 0$, $\ln\gamma = \text{constant}$ (Henry's Law). Furthermore, the two activity coefficients must conform to the Gibbs-Duhem equation

$$X_{mt}\left(\frac{\partial \ln\gamma_{mt}}{\partial X_{mt}}\right)_{P,T} + X_{hc}\left(\frac{\partial \ln\gamma_{hc}}{\partial X_{mt}}\right)_{P,T} = 0$$

If the power series are limited to three terms, this requires the following relationship between the constants (see Denbigh 1966, p. 240):

$$\lambda_{mt} = \lambda_{hc} = 0$$

$$\alpha_{hc} = \alpha_{mt} + 3/2\beta_{mt}$$

$$\beta_{hc} = -\beta_{mt}$$

Designating $\ln\gamma_{mt}$ at $X_{mt} = 0$ by M and $\ln\gamma_{hc}$ at $X_{hc} = 0$ by H, it follows that

$$M = \alpha_{mt} + \beta_{mt}$$

$$H = \alpha_{hc} + \beta_{hc} = \alpha_{mt} + \tfrac{1}{2}\beta_{mt}$$

Following the method of Carlson & Colburn (1942), it is possible to express the constants in the two power series in terms of M and H :

$$\ln\gamma_{mt} = (2H - M)(1 - X_{mt})^2 + 2(M - H)(1 - X_{mt})^3$$

$$\ln\gamma_{hc} = (2M - H)(1 - X_{hc})^2 + 2(H - M)(1 - X_{hc})^3$$

If two solutions are at equilibrium, the chemical potential of each component must be equal in the two phases :

$$\mu_{mt}{}^{I} = \mu_{mt}{}^{II}$$

$$\mu_{hc}{}^{I} = \mu_{hc}{}^{II}$$

or

$$\mu^*_{mt} + RT\ln(\gamma X)^{I}_{mt} = \mu^*_{mt} + RT\ln(\gamma X)^{II}_{mt}$$

$$\mu^*_{hc} + RT\ln(\gamma X)^{I}_{hc} = \mu^*_{hc} + RT\ln(\gamma X)_{hc}$$

where μ^*_{mt} is the chemical potential of pure $Fe_{0.5}FeO_2$ with an inverse structure and μ^*_{hc} is the chemical potential of pure $Fe_{0.5}AlO_2$ with a normal structure. Because μ^*_{mt} and μ^*_{hc} cancel and $X_{mt} = 1 - X_{hc}$, the equations reduce to :

$$\ln(1 - X^{I}_{hc}) + \ln\gamma^{I}_{mt} = \ln(1 - X^{II}_{hc}) + \ln\gamma^{II}_{mt}$$

$$\ln X^{I}_{hc} + \ln\gamma^{I}_{hc} = \ln X^{II}_{hc} + \ln\gamma^{II}_{hc}$$

Substituting the power series expressions for the $\ln\gamma$ terms, the following equations are obtained :

$$\ln(1 - X^{I}_{hc}) + [(2H - M)(X_{hc})^2 + 2(M - H)(X^{I}_{hc})^3]$$
$$= \ln(1 - X^{II}_{hc})^2 + [(2H - M)(X^{II}_{hc})^2 + 2(M - H)(X^{II}_{hc})^3]$$

$$\ln X^{I}_{hc} + [(2M - H)(1 - X^{I}_{hc})^2 + 2(H - M)(1 - X^{I}_{hc})^3]$$
$$= \ln X^{II}_{hc} + [(2M - H)(1 - X^{II}_{hc})^2 + 2(H - M)(1 - X^{II}_{hc})^3]$$

These two simultaneous equations may be solved for H and M at various temperatures and at 2 kb because the compositions of the two coexisting phases, X^{I}_{hc} and X^{II}_{hc}, are known from the solvus determined by Turnock & Eugster (1962). It was found that, in the temperature range 600-900°C, H and M vary linearly with 1/T (T in °K), as follows :

$$H = \frac{2570}{T} - 0.56$$

$$M = \frac{2740}{T} - 0.26$$

Knowing *H* and *M* at any given temperature, it is possible to calculate the variation of the activity coefficients and of the activities with composition (Figs. 1 and 2). It is obvious that fixing the activity of one component also determines the activity of the other component. Solutions having compositions in the range of the miscibility gap are not stable; the corresponding activities are shown as dotted lines in Figure 2.

It has been pointed out by Green (1970) that the values of activity coefficients derived from phase diagrams depend on the solution model. At present, there is no guidance available from thermochemical data in the choice of a solution model for magnetite-hercynite solid solutions. Although the two-constant Margules model may not be the most appropriate, it has the advantage of simplicity.

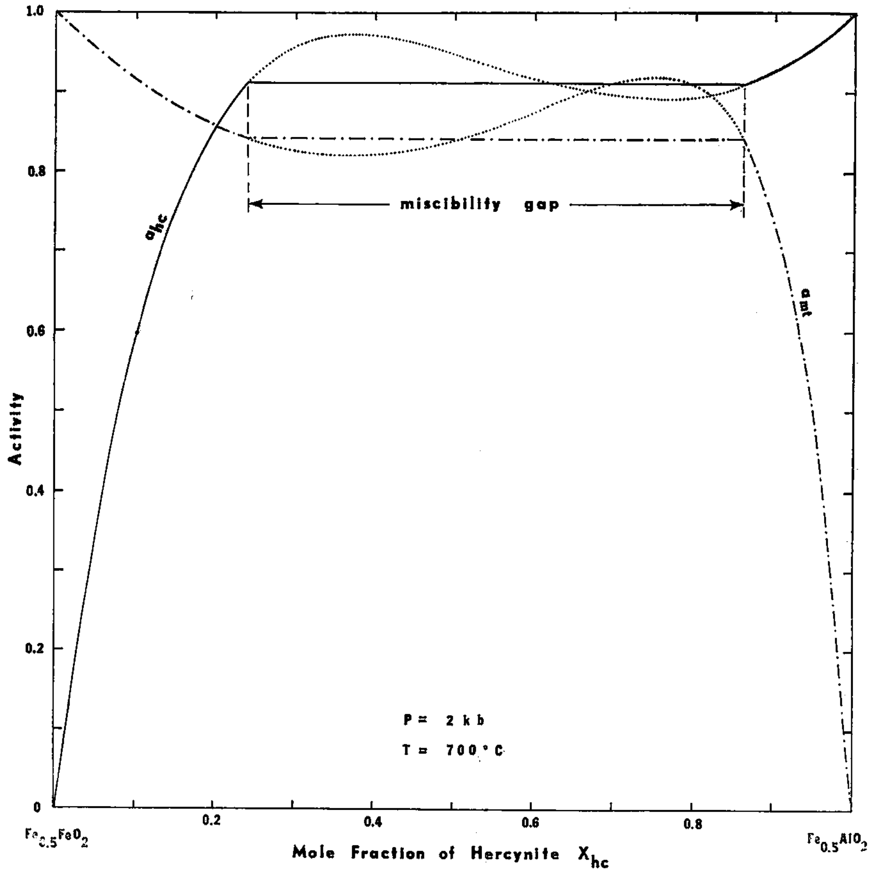

FIG. 2. Variation of activities with composition.

EXPERIMENTAL WORK IN THE SYSTEM SiO_2-Al_2O_3-FeO-O

Various phase relations in this system have been determined experimentally at oxygen fugacities controlled by buffers. In the present paper, oxygen fugacities have been calculated according to formulas given by Eugster & Wones (1962) for magnetite-wustite, by Wones & Gilbert (1969) for quartz-fayalite-magnetite, and by Huebner & Sato (1970) for nickel-nickel oxide. The experimental results are listed in Table 1.

Because all experimental work was carried out at a pressure of 2 kb, it is convenient for subsequent calculations to define the standard state of solids as the pure substance at a pressure of 2 kb. The standard state of oxygen, however, remains at a fugacity of one bar. The standard free energy change $\Delta G°$, for various reactions, at a given temperature, was calculated from the relationship

$$\Delta G° = -RT \ln K$$

where K is the equilibrium constant expressed in fugacities and activities.

Reactions referred to in this paper are listed in Table 2. All phases, except magnetite and hercynite, are regarded as pure substances. Therefore, the equilibrium constants are expressions of only three variables at the most, the fugacity of oxygen and the activities of $Fe_{0.5}FeO_2 (a_{mt})$ and of $Fe_{0.5}AlO_2 (a_{hc})$. The appropriate form of each equilibrium constant is apparent from the reaction equation. Cordierite has been treated as an anhydrous phase because water is present as molecular H_2O rather than in the form of bonded (OH) groups (Schreyer & Yoder 1964).

Hsu (1968) reports the invariant point quartz-almandine-hercynite-cordierite-fayalite at 875°C and at an oxygen fugacity slightly higher than that of the magnetite-wustite buffer. Accepting a value of $\log f_{O_2} = -15.2$, the activity of $Fe_{0.5}FeO_2$ in the spinel phase may be obtained from reaction (1), $\Delta G°$ of this reaction being known from the data of Wones

TABLE 1. EXPERIMENTAL DATA IN THE SYSTEM SiO_2-Al_2O_3-FeO-O (at 2 kb)

Coexisting phases	T°C	Oxygen buffer	Reference
quartz–almandine–hercynite–cordierite–fayalite	875	~ MW	Hsu (1968)
quartz–almandine–hercynite–magnetite	727	QFM	Hsu (1968)
quartz–almandine–hercynite–cordierite–magnetite	700	~ QFM	Rutherford & Eugster (1967)
quartz-sillimanite–hercynite-cordierite	875	QFM	Richardson (1968)
	750	NMO	Rutherford (1970)

TABLE 2. STANDARD FREE ENERGY CHANGES

	Reactions	T°C	$\log f_{O_2}$	a_{mt}	a_{hc}	$\Delta G^\circ = -RT \ln K$
(1)	$\frac{4}{3}Fe_{0.5}FeO_2 + SiO_2 \rightleftarrows Fe_2SiO_4 + \frac{1}{3}O_2$	875	—15.20	.328		38,950 —13.7 T
(2)	$Fe_3Al_2Si_3O_{12} + \frac{1}{3}O_2 \rightleftarrows 2Fe_{0.5}AlO_2 + \frac{4}{3}Fe_{0.5}FeO_2 + 3SiO_2$	875	—15.20	.328	.956	—33,460 + 9.1 T
		727	—16.56	.832	.902	
(3)	$2Fe_{0.5}AlO_2 + \frac{5}{2}SiO_2 \rightleftarrows FeAl_2Si_{2.5}O_9$	875			.956	— 1,240 + 0.9 T
		700			.911	
(4)	$6Fe_{0.5}AlO_2 + \frac{1}{2}O_2 + 3SiO_2 \rightleftarrows 2Fe_{0.5}FeO_2 + 3Al_2SiO_5$	875	—13.26	.328	.956	—66,180 +31.2 T
		750	—14.92	.670	.924	
(5)	$6Fe_{0.5}AlO_3 + 5SiO_2 \rightleftarrows Fe_3Al_2Si_3O_{12} + 2Al_2SiO_5$					—10,660 +11.7 T
(6)	$Fe_2SiO_4 + Fe_3Al_2Si_3O_{12} + \frac{2}{3}O_2 \rightleftarrows 2Fe_{0.5}AlO_4 + \frac{8}{3}Fe_{0.5}FeO_2 + SiO_2$					—72,410 +22.8 T
(7)	$Fe_2SiO_4 + FeAl_2Si_{2.5}O_9 + \frac{1}{3}O_2 \rightleftarrows \frac{4}{3}Fe_{0.5}FeO_2 + 2Fe_{0.5}AlO_2 + \frac{7}{2}SiO_2$					—37,710 +12.8 T
(8)	$Fe_3Al_2Si_3O_{12} + \frac{1}{2}SiO_2 \rightleftarrows Fe_2SiO_4 + FeAl_2Si_{2.5}O_9$					4,250 — 3.7 T
(9)	$Fe_3Al_2Si_3O_{12} + \frac{1}{3}O_2 \rightleftarrows FeAl_2Si_{2.5}O_9 + \frac{4}{3}Fe_{0.5}FeO_2 + \frac{1}{2}SiO_2$					—34,700 +10.0 T
(10)	$Fe_3Al_2Si_3O_{12} + 2Al_2SiO_5 + \frac{5}{2}SiO_2 \rightleftarrows 3FeAl_2Si_{2.5}O_9$					6,940 — 9.0 T
(11)	$Fe_3Al_2Si_3O_{12} + \frac{1}{2}O_2 \rightleftarrows 2Fe_{0.5}FeO_4 + Al_2SiO_5 + 2SiO_2$					—55,520 +19.5 T
(12)	$FeAl_2Si_{2.5}O_9 + \frac{1}{6}O_2 \rightleftarrows \frac{2}{3}Fe_{0.5}FeO_2 + Al_2SiO_5 + \frac{3}{2}SiO_2$					—20,820 + 9.5 T

& Gilbert (1969). Since the activity-composition relations for both components have been calculated, this also determines the activity of $Fe_{0.5}AlO_2$. Knowing $\log f_{O_2}$ and the activities of $Fe_{0.5}FeO_2$ and $Fe_{0.5}AlO_2$ at 875°C, it is possible to calculate $\Delta G°$ of reaction (2). Hsu (1968) equilibrated quartz + almandine + hercynite + magnetite at 727°C and $\log f_{O_2}$ defined by the quartz-fayalite-magnetite buffer. The coexistence of hercynite and magnetite determines their composition and, therefore, the activities of both components. Thus $\Delta G°$ of reaction (2) may be calculated at 727°C.

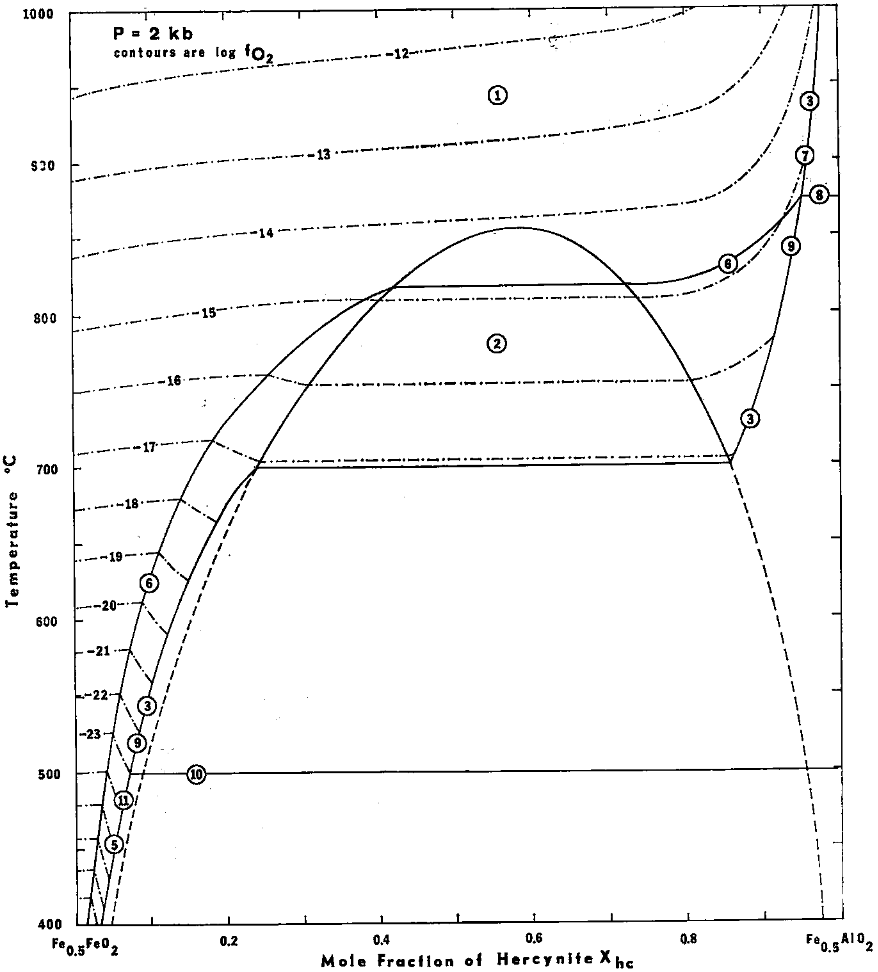

FIG. 3. Equilibria at relatively low oxygen fugacity.

Rutherford & Eugster (1967) report the invariant point quartz-almandine-hercynite-cordierite-magnetite at 700°C. Again, the coexistence of magnetite and hercynite determines the activities of $Fe_{0.5}FeO_2$ and $Fe_{0.5}AlO_2$. The assemblage quartz-hercynite-cordierite observed at 875°C and 700°C allows the calculation of $\Delta G°$ of reaction (3) at these two temperatures.

From $\Delta G°$ of reaction (3), the activity of $Fe_{0.5}AlO_2$ may be calculated at 750°C; this also determines the activity of $Fe_{0.5}FeO_2$. Quartz, silli-

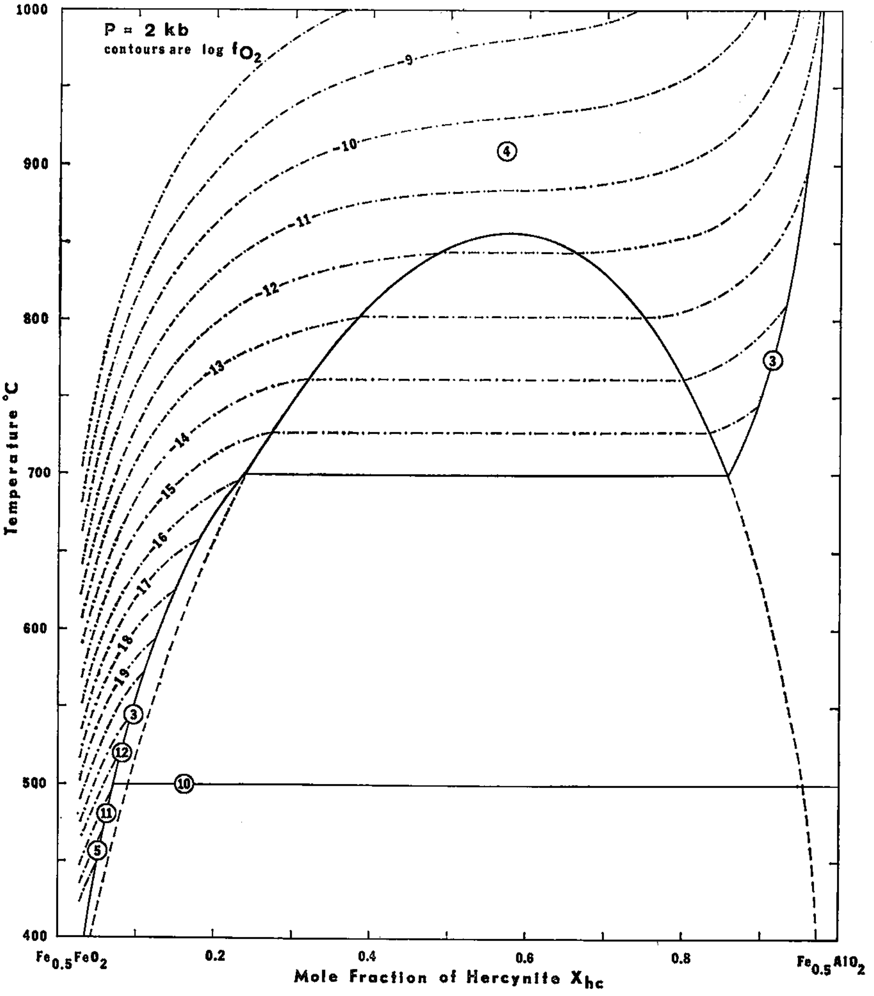

FIG. 4. Equilibria at relatively high oxygen fugacity.

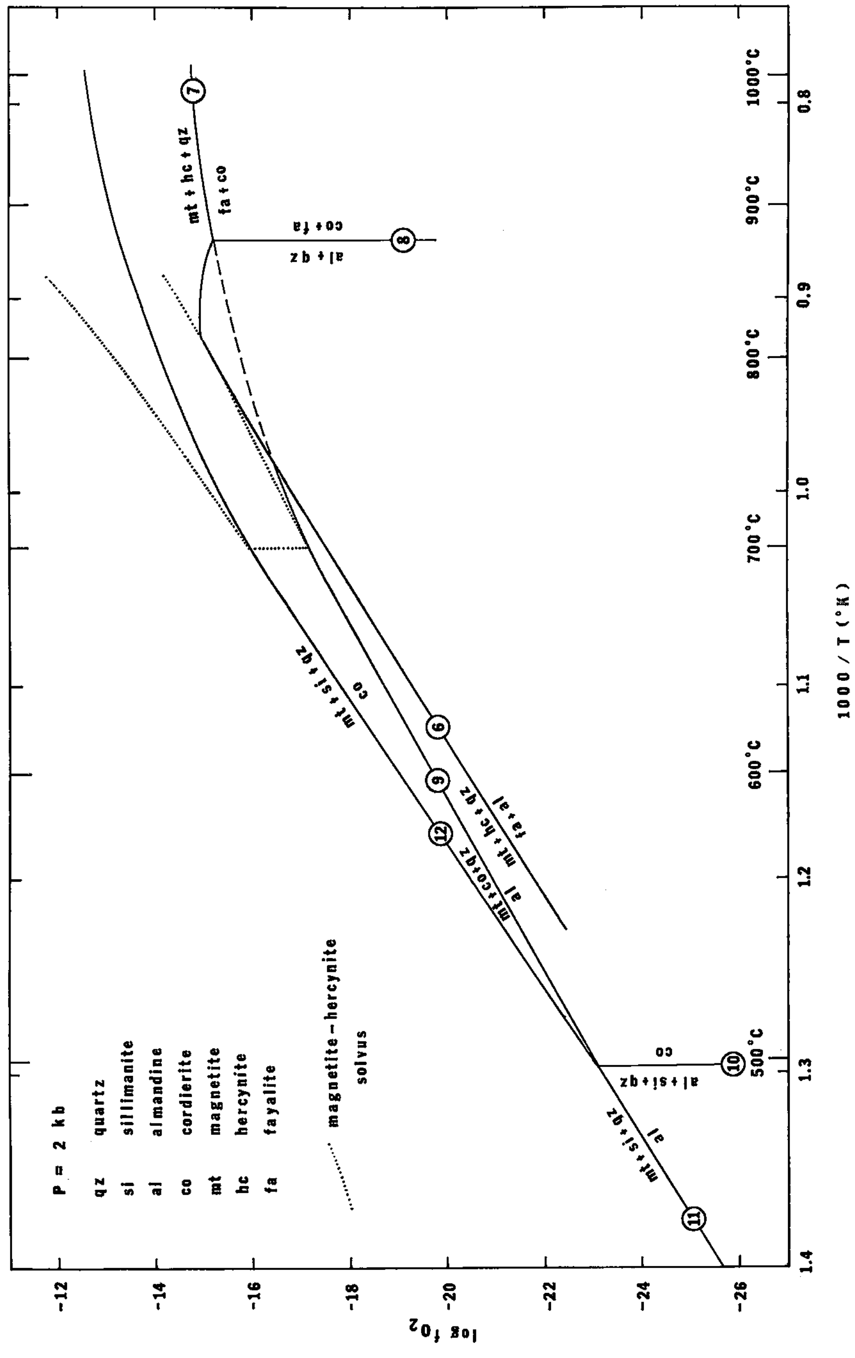

FIG. 5. Equilibria in the system SiO_2-Al_2O_3-FeO-O in presence of quartz.

manite, hercynite, and cordierite coexist at 875°C and $\log f_{O_2}$ defined by the quartz-fayalite-magnetite buffer (Richardson 1968) and at 750°C and $\log f_{O_2}$ defined by the nickel-nickel oxide buffer (Rutherford 1970). This permits the calculation of $\Delta G°$ of reaction (4) at these two temperatures. Reaction (5) is obtained by combining reactions (2) and (4).

Reactions (1) to (5) may be shown on T-X diagrams, plotting temperature against spinel composition (Figs. 3 and 4). Reactions (1), (2), and (4) are represented by contours of $\log f_{\ 2}$ in a field. Reactions (3) and (5) plot as lines, limiting the stability of spinel in the presence of quartz.

CALCULATED PHASE RELATIONS

The standard free energy changes derived for reactions (1) to (4) from experimental data are based on the assumption that $\Delta G°$ of a reaction varies linearly with temperature and that the spinel solid solutions conform to the imposed solution model. Other reactions of interest, e.g. (5) to (12), are linear combinations of reactions (1) to (4). The equilibrium temperatures of reactions (6) to (12) at specified values of $\log f_{O_2}$ may be obtained from various intersections between reactions (1) to (5) shown in Figures 3 and 4. Thus reactions (6) to (12) are readily transposed to a diagram of $\log f_{O_2}$ plotted against 1/T (Fig. 5). Also shown on this diagram is the spinel solvus. It is interesting to note that at high temperatures, cordierite is stabilized relative to almandine + sillimanite + quartz, in contrast to direct experimental determination (Richardson 1968).

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