

A. J. H. BOERBOOM*, J. KISTEMAKER

**Mass Spectrometric Determination and Thermodynamic Calculation
of the Equilibria Between Iron, Carbon and Oxygen**

INTRODUCTION

The reduction of iron ore to iron is one of the oldest chemical techniques. It marked the start of a new era in the prehistory of mankind: the iron age. Nowadays it is the second-largest human generated chemical process on earth. It amounts to quantities of the order of 2 million tons per day and is surpassed only by the burning of coal for the generation of heat.

An enormous body of scientific literature exists on this process dealing with technical and chemical aspects. However, a complete survey, which could be used to comprehend all measurements, does not exist.

Thermodynamics, however, enables one to calculate the equilibrium between a number of chemical compounds in an entire temperature and pressure region, if only a limited set of data, e.g. free energy and entropy, of these compounds are known. The latter data should be provided by other means. Among others, mass spectrometric determination of some equilibria between these compounds can provide the desired data. We will give the necessary thermodynamic formulae, derived from fundamental principles. A relatively small number of mass spectrometric measurements will give the complete set of equilibria between iron, iron oxides, iron carbonate, graphite (carbon) or cementite (Fe_3C), and a CO-CO_2 mixture.

THERMODYNAMIC CONSIDERATIONS

We will investigate a thermodynamic system consisting of a number of chemical compounds A, in equilibrium at a certain temperature and pressure, and as virtual

* Present address: Albrecht Dürerstraat 25", 1077 LT Amsterdam, the Netherlands.

process a small change δn_i in the quantities of these compounds with the condition $\delta n_i = 0$, thus a chemical reaction.

For this system the thermodynamic potential

$$G = U - TS + PV$$

is a minimum, so $\partial G_{T,P} \leq n_i = 0$;

$$\begin{aligned} dU &= TdS - PdV + \sum \mu_i dn_i \text{ with } \mu_i = (\partial U / \partial n_i)_{S, V, n_{k \neq i}} \\ dG &= dU - TdS - SdT + PdV + VdP \\ &= -SdT + VdP + \sum \mu_i dn_i \end{aligned} \quad (1)$$

$$\partial G_{T,P, \sum n_i} = 0 = \sum \mu_i \partial n_i \text{ with } \sum \partial n_i = 0. \quad (2)$$

This is the equilibrium condition. To derive the equilibrium state from this equation, we have to calculate μ_i as a function of T, P , and n_k . From (1) we see that

$$\mu_i = (\partial G / \partial n_i)_{T, P, n_{k \neq i}}.$$

Consequently, we first calculate G :

$$G(T, P, n_k) = G(T_0, P_0, n_k) + \int_{T_0}^T (\partial G / \partial T)_{P_0, n_k} dT + \int_{P_0}^P (\partial G / \partial P)_{T, n_k} dP.$$

Again from (1) we see that $(\partial G / \partial P)_{T, n_k} = V(T, P, n_k)$ and $(\partial G / \partial T)_{P_0, n_k} = -S(T, P_0, n_k) = -S(T_0, P_0, n_k) - \int_{T_0}^T (\partial S / \partial T)_{P_0, n_k} dT$
 $(\partial S / \partial T)_{P_0, n_k} = \frac{1}{T} (\partial W / \partial T)_{P_0, n_k} = C_P / T$, where C_P equals the total specific heat of the system. So finally,

$$\begin{aligned} G(T, P, n_k) &= G(T_0, P_0, n_k) - (T - T_0)S(T_0, P_0, n_k) + I_1 + I_2 \\ &= W(T_0, P_0, n_k) - TS(T_0, P_0, n_k) + I_1 + I_2 \end{aligned} \quad (3)$$

with $I_1 = \int_{P_0}^P V(T, P, n_k) dP$, $I_2 = \int_{T_0}^T \int_{T_0}^t \frac{C_P(\tau, P_0, n_k)}{\tau} d\tau dt$ and $W = U + PV =$ enthalpy.

In case the solids do not mix and the pressure P_0 is sufficiently low, equation (3) becomes very simple. We substitute:

$$\begin{aligned} W(T_0, P_0, n_k) &= \sum n_i w_i(T_0, P_i), \\ S(T_0, P_0, n_k) &= \sum n_i s_i(T_0, P_i) - R \sum n_g \ln n_g, \\ C_P(t, P_0, n_k) &= \sum n_i c_{P_i}(t), \\ PV(T, P, n_k) &= \left(\sum n_g \right) \{ RT + B(T, n_k)P + C(T, n_k)P^2 + \dots \}. \end{aligned}$$

Here the lesser characters w, s, c_P indicate enthalpy, entropy, and specific heat per mole and the index g means that only should be summed over the gaseous

compounds. For solids $P_i = P_0$ but for gaseous compounds $P_i = (n_i / \sum n_j) P_0$. Also for solids equations of state in the shape

$$V_k = n_k \{ B_k(T) + C_k(T)P + \dots \}$$

exist but, as long as we work with relatively low pressures, we may neglect the volume of the solid in comparison with the gas volume. Now we consider a chemical reaction between the compounds of the system with the reaction equation

$$\sum m_i A_i = \sum m_k A_k.$$

The quantities ∂n_i in (2) are proportional with the m_i and m_k from this equation. Consequently, (2) transforms into

$$\begin{aligned} \sum m_i \mu_i &= 0 = \sum m_i (\partial G / \partial n_i)_{T, P, n_i \neq k} \\ &= \sum m_i \left\{ w_i(T_0, P_i) - T_{S_i}(T_0, P_i) - \int_{T_0}^T \int_{T_0}^t c_{P_i}(\tau) / \tau d\tau dt \right\} + \\ &+ \sum \left\{ RT m_j (1 + \ln n_j) + m_j \int_{P_0}^P (\partial V / \partial n_j)_{T, P, n_k \neq j} dp \right\}. \end{aligned}$$

Now we define the equilibrium constant through $\ln K_P = \sum m_j \ln P_j$, where P_j stands for the partial pressure of component j : $P_j = m_j / \sum m_l P$ and the equilibrium constant becomes

$$\begin{aligned} RT \ln K_P - RT \ln K_{P_0} &= \\ \sum m_i \left\{ -w_i(T_0, P_i) + T_{S_i}(T_0, P_i) + \int_{T_0}^T \int_{T_0}^t c_{P_i}(\tau) / \tau d\tau dt \right\}. \end{aligned} \quad (4)$$

For an ideal gas w is independent of the pressure. Moreover, $s(T, P_1) - s(T, P_2) = R \ln P_2 - R \ln P_1$. Consequently,

$$RT \ln K_P = \sum m_l \left\{ -w_l(T_0, 1) + T_{S_l}(T_0, 1) + \int_{T_0}^T \int_{T_0}^t c_{P_l}(\tau) / \tau d\tau dt \right\}.$$

In this shape we will apply the equilibrium constant. The expression, however, can be brought in another shape where, besides the pressure P_0 , also the temperature T_0 has been eliminated:

Partial integration of the integral term yields

$$\int_{T_0}^T \int_{T_0}^t C_P / \tau d\tau dt = \left[t \int_{T_0}^t C_P / \tau d\tau \right]_{T_0}^T - \int_{T_0}^T t C_P / t dt = T \int_{T_0}^T C_P / t dt - \int_{T_0}^T C_P dt.$$

Now $C_P = (\partial w / \partial T)_P$ and $C_P / T = (\partial s / \partial T)_P$. Consequently, we find after substitution into (4)

$$RT \ln K_P / K_{P_0} = \sum m_l \{ -w_l(T, P_l) + T_{S_l}(T, P_l) \} = - \sum m_l g_l(T, P_l).$$

By a similar transformation as before, P_0 can be eliminated again and we obtain finally

$$RT \ln K_P = - \sum m_i g_i(T, 1) = -\Delta g_P(T),$$

where Δg_P represents the difference of the thermodynamic potentials of the compounds at the left hand side and right hand side, respectively, in the reaction equation, at the temperature T and each compound at unit pressure.

THE QUANTITIES c_p , w , s AND THE VIRAL COEFFICIENTS

Kelley [1] gives the specific heat of many substances, among which all species of interest for the Fe-C-O system, in the shape $c_p = a + bT + cT^2 + dT^{-1/2} + eT^{-2}$ cal/mol degree (see Table 1).

This expression gives a good representation of the specific heats over large temperature regions and makes analytical integration of equation (4) possible.

Table 1. The specific heat of some compounds of Fe, C and O

compound	a	$b \cdot 10^3$	$c \cdot 10^6$	d	$e \cdot 10^{-5}$	Temp. K	$\pm\%$
α -Fe	3.90	6.80	-	-	-	272 - 1033	1
β -Fe	9.85	-	-	-	-	1033 - 1183	2
γ -Fe	7.55	1.14	-	-	-	1179 - 1674	3
FeO	12.62	1.492	-	-	-0.762	298 - 1173	$2\frac{1}{2}$
Fe ₃ O ₄	41.17	18.82	-	-	-9.795	273 - 1065	2
Fe ₂ O ₃	24.72	16.04	-	-	-4.234	273 - 1100	2
Fe ₃ C	21.55	15.06	-	-	-	273 - 463	3
Fe ₃ C	27.01	1.46	-	-	-	463 - 1026	3
FeCO ₃	11.63	26.8	-	-	-	298 - —	6
C _{graph}	9.06	-0.13	-	-121	-	298 - 1600	$2\frac{1}{2}$
C _{diam}	-1.97	13.33	-6.29	-	-	298 - 1100	$2\frac{1}{2}$
CO	6.42	1.655	-0.196	-	-	298 - 1500	$1\frac{1}{2}$
CO ₂	6.21	10.40	-3.545	-	-	298 - 1500	2
O ₂	9.85	0.22	-	-54.5	-	298 - 2500	$2\frac{1}{2}$

Second and higher virial coefficients of CO and CO₂ are given in literature [2], and of CO-CO₂ mixtures have been calculated and measured by Boerboom *et al.* [3].

However, as we are only interested in the general structure of the Fe-C-O system, we will neglect these complications and assume the ideal gas law valid also in the domain of higher pressures.

IRON, CARBON, OXYGEN AND THEIR COMPOUNDS

Iron has various phases. Below 768°C α -iron is stable. At 768°C a second-order phase change terminates. There iron loses its ferro-magnetic properties: its crystallographic state remains unaffected, so there is no heat of reaction involved,

but a difference in specific heat should be taken into account. We may call iron above 768°C β -iron.

At 906°C a change to γ -iron takes place. This is a first-order phase change to a different crystallographic state and is associated with a heat of reaction. Carbon dissolves in appreciable quantities in γ -iron. This decreases the transition temperature down to the eutectic temperature at 733°C where γ -iron is in equilibrium with graphitic carbon or down to the eutectic at 723°C where it is metastable equilibrium with cementite (Fe_3C). At 1401°C pure iron transforms to δ -iron, which is crystallographically identical with γ -iron. This transition temperature is increased by dissolved carbon, see Fig. 1.

We will only consider the graphite modification of carbon in our calculations. Oxygen almost exclusively appears in the Fe-C-O-system in contact with the highest oxidation states: Fe_2O_3 and CO_2 . Only at very high temperatures these compounds dissociate in considerable quantities. Cementite (Fe_3C) is metastable, it dissociates at high temperature into Fe and C. At very high pressure, however, Fe_3C becomes stable as formation of Fe_3C from $\text{Fe} + \text{C}$ is accompanied with decrease of volume. In our calculations we neglect the volume of the solid phase so we cannot find this effect.

Iron has three oxides: Fe_2O_3 and Fe_3O_4 , with a fixed stoichiometric composition, and ferrous oxide with a composition between $\text{Fe}_{0.83}\text{O}$ and $\text{Fe}_{0.95}\text{O}$ depending on the oxidation potential of the surrounding phases, see Fig. 2.

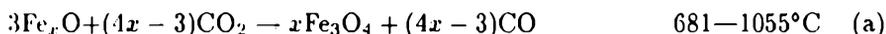
There are several iron carbonates but only FeCO_3 is of importance for us. Several iron-carbonyl compounds $\text{Fe}(\text{C}'\text{O})_n$ — ($n = 3, 4, 5$) are known. They are stable if the pressure is higher than the dissociation pressure (though not stable with respect to $\text{C} + \text{CO}_2$ as carbon monoxide is not stable with respect to $\text{C} + \text{CO}_2$). This pressure is, however, much too high in the temperature region of our calculations, so we will not consider these compounds. Carbon has three oxides: CO, CO_2 and C_2O_3 (oxalic acid anhydrid). The latter compound, however, dissociates at higher temperatures so it is not of interest for us. For the same reason we will not discuss ferrous and ferric oxalate. Summarizing: we will consider the equilibria between Fe, FeO, Fe_3O_4 , Fe_2O_3 , C, CO, CO_2 , Fe_3C and FeCO_3 .

When phases have not a constant composition we will write Fe_xO for ferrous oxide in our equations. In the same way we write FeC_y for iron containing carbon and CO_z for the CO- CO_2 mixture.

First, we will calculate the stable diagram, where we will assume that the pressure is low enough to avoid appearance of FeCO_3 . After this we calculate the metastable diagram with Fe_3C , as a metastable phase, instead of C. Finally, we will consider the changes caused by the appearance of FeCO_3 .

MEASUREMENTS

We investigated the following equilibria over the temperature regions indicated:



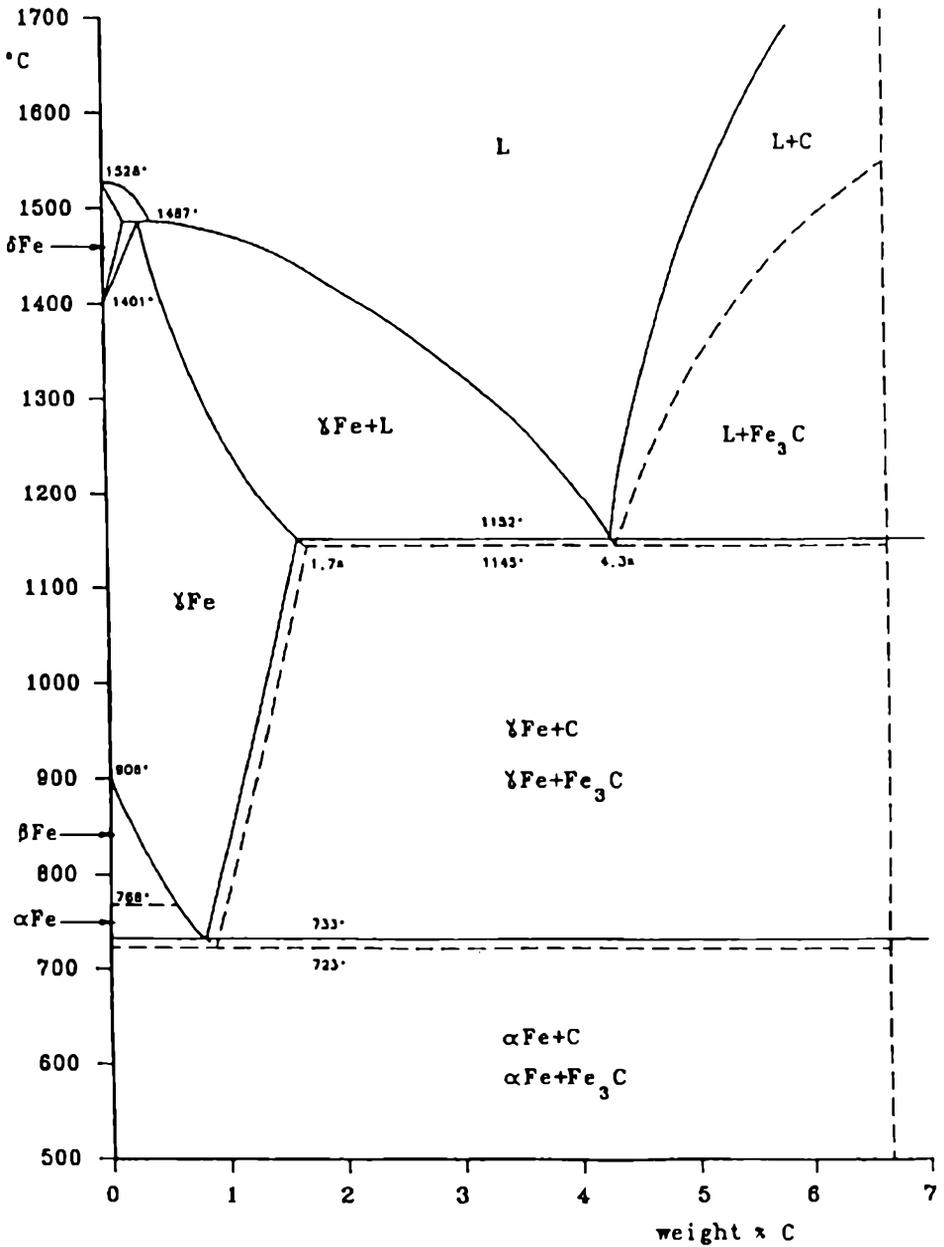


Fig. 1. The iron-carbon diagram. Full lines: the stable diagram, dotted lines: the meta-stable diagram

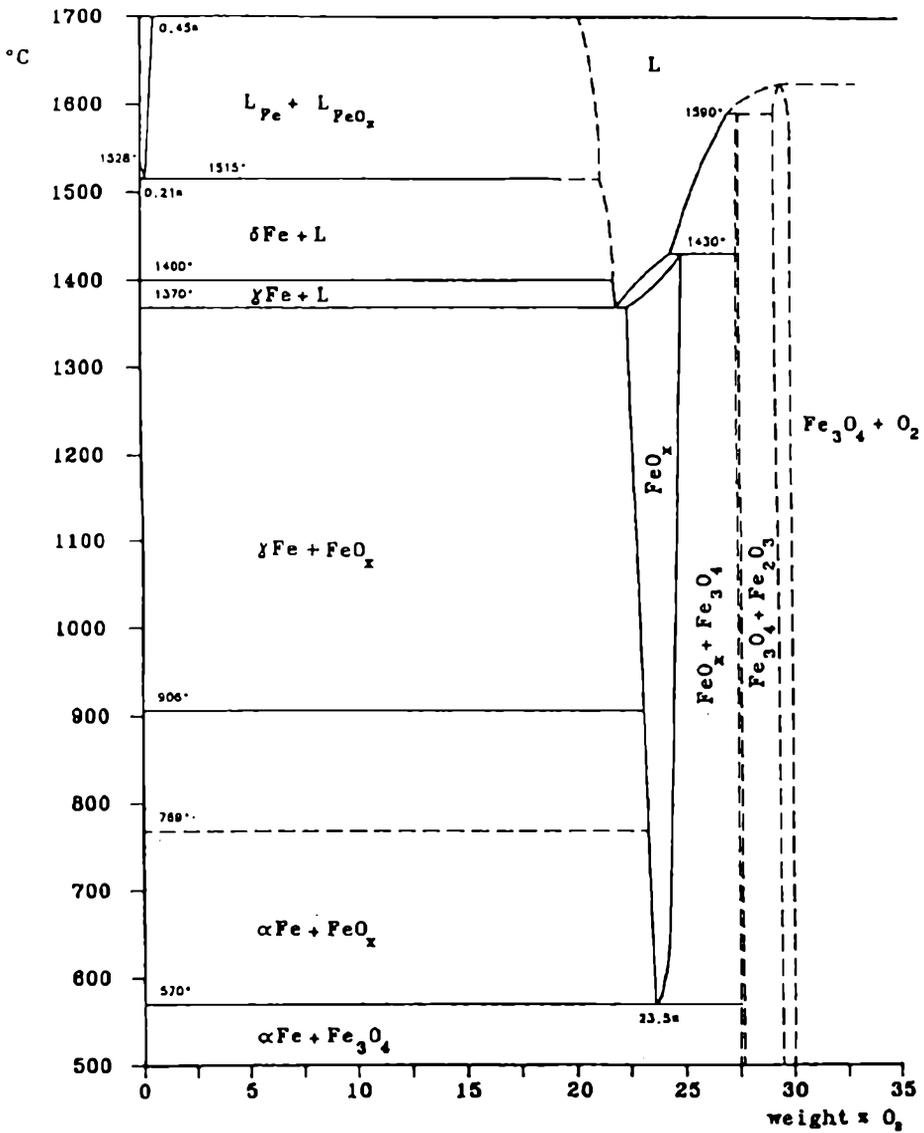
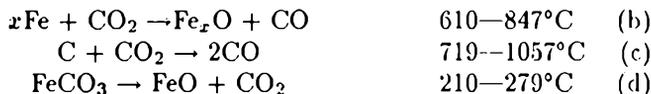


Fig. 2. The iron-oxygen diagram, showing the variable composition of ferrous oxide



Measuring at lower temperatures was limited by the reaction rate being too slow, at higher temperatures by the melting point of copper (1083°C); in case (d) the limitation was the dissociation pressure of FeCO_3 . Measurements of equilibrium (c) were advanced by adding Ni-powder as a catalyst.

Though some of these equilibria have been measured already by other investigators, we applied our new method on all above reactions to get uniform results.

PREPARATION OF THE COMPOUNDS AND TECHNIQUE OF THE MEASUREMENTS

High purity iron was used in our measurements as small amounts of impurities greatly influence the equilibrium concentrations. Especially the absence of Mn was verified as this element forms mixed crystals with iron. Already in extreme low concentrations the redox potential is lowered considerably and thus the equilibria are greatly influenced. Ferrous oxide (FeO) was obtained by pyrolysis of ferrous oxalate [4].

Oxidation of FeO with air at 400°C led to Fe_2O_3 and reduction of this compound with moist hydrogen gave Fe_3O_4 .

FeCO_3 was made by the reaction $\text{FeSO}_4 + \text{CaCO}_3 \rightarrow \text{FeCO}_3 + \text{CaSO}_4$ at 120°C in aquatic solution in a closed vessel under pressure. The presence of CaSO_4 does not interfere in the measurements of the dissociation pressure of FeCO_3 .

A very pure carbon was obtained as graphite from Le Carbone Lorraine. It was not possible to obtain cementite (Fe_3C) of sufficient purity.

Table 2. The mass spectra of CO and CO_2

m/e ion	12 C^+	14 CO^{++}	16 O^+	22 CO_2^{++}	28 CO^+	32 O_2^+	44 CO_2^+
CO_2	12600	-	9700	1020	12300	146	104500
CO	7060	1580	3900	-	148000	-	...

Standard samples of CO- CO_2 mixtures were prepared by accurate mixing of CO and CO_2 of analytic quality. Precision measurements of the CO/ CO_2 ratio were performed on a home built single focusing mass spectrometer for isotope abundance measurements [5]. In Table 2 the spectra of pure CO and of pure CO_2 are given. As could be expected, mass $m/e = 44$ is excellent for CO_2 and $m/e = 28$ can be used for CO if we apply a small correction for CO^+ originating from CO_2 . For low CO-contents ($< 1\%$) peak 14 (CO^{++}) gives more precise results. Peak 40 (Ar^+) was used to check the absence of air leakage (interference of N_2^+ at mass 28).

The desired mixture of the pure phases of Fe, FeO , Fe_3O_4 , Fe_2O_3 and C was put in a pure copper vessel and this vessel was closed by welding. The set-up is shown in Fig. 3.

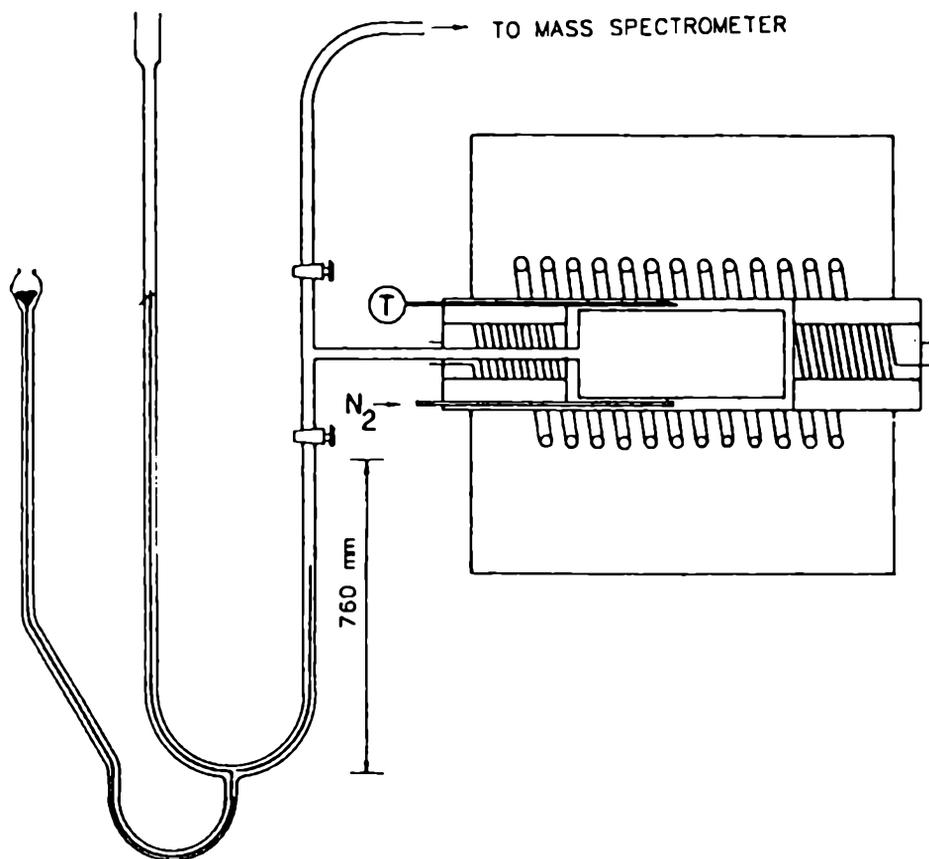


Fig. 3. The experimental set-up. A vessel made of pure copper, is heated in a thermostat. The vessel is filled with iron, iron oxide or iron carbonate and welded, so that no seal is necessary. A mixture of CO and CO₂ is admitted. After the equilibrium has been established, temperature, gas pressure and gas composition are measured. Nitrogen gas is used to shield the hot copper from atmospheric oxygen

Most equilibria were attained from both higher as well as lower temperatures; the results are given in Fig. 4.

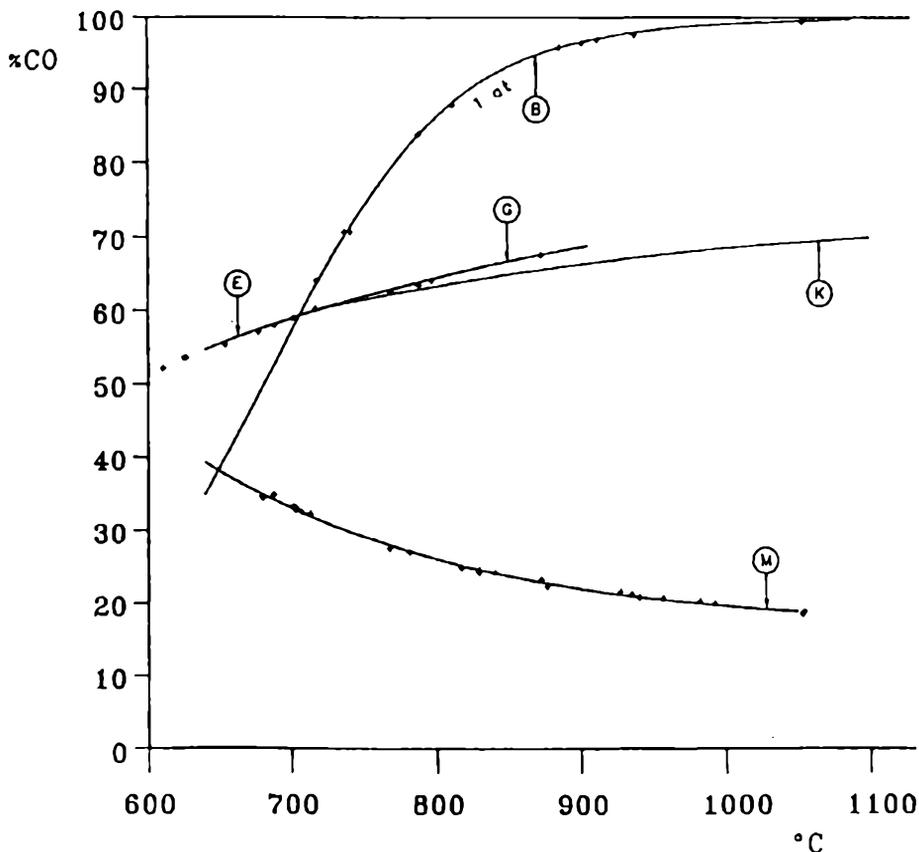


Fig. 4. Compilation of the measurements. Full lines were obtained by applying a least-squares method on the measuring points. The equilibria (a) and (b) are independent of pressure, the measurements of equilibrium (c) were reduced to the pressure of 1 atmosphere

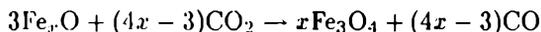
THE 5-PHASE POINT $\alpha\text{Fe}-\text{FeO}-\text{Fe}_3\text{O}_4-\text{C}-\text{CO}_2$

The equilibria $\text{C}-\text{CO}_2$, $\alpha\text{Fe}-\text{FeO}-\text{CO}_2$ and $\text{FeO}-\text{Fe}_3\text{O}_4-\text{CO}$, measured above, have two degrees of freedom so to produce planes in the P, T, z -space. The planes describing the first two equilibria can be determined from our measurements:

$$2 \log P_{\text{CO}} - \log P_{\text{CO}_2} = -8962/T + 9.003 - 2.43A - 6.96B + 3.15C + 121D$$

$$\log P_{\text{CO}} - \log P_{\text{CO}_2} = -999/T + 0.958 + 8.39A - 14.05B + 3.35C - 0.76E.$$

The third equilibria needs some correction as ferrous oxide is not exactly stoichiometric but has the formula Fe_xO where x can be found in literature [6], see also Fig. 3. The reaction formula reads



and the equilibrium can be described with

$$\log P_{\text{CO}} - \log P_{\text{O}_2} = 2527/T + 3.211 + 3.52A + 5.60B + 3.35C - 7.51E.$$

The first equilibrium depends on the pressure and forms a wave-like plane in the P, T, z -space. In Table B and Fig. 5 some intersections with various planes $P = \text{constant}$ are given.

The second and third equilibria are independent of pressure, so the planes are perpendicular to the T, z -plane.

The intersection of each pair of these planes produces a 4-phase-line viz. $\alpha\text{Fe}-\text{FeO}-\text{C}-\text{CO}_2$, $\text{Fe}-\text{Fe}_3\text{O}_4-\text{C}-\text{CO}_2$ and $\alpha\text{Fe}-\text{Fe}_3\text{O}_4-\text{C}-\text{CO}_2$, respectively: Tables E, M and D.

These 4-phase-lines are represented by the two equations of the intersecting planes. The three 4-phase-lines intersect in a single point: the 5-phase-point $\alpha\text{Fe}-\text{FeO}-\text{Fe}_3\text{O}_4-\text{C}-\text{CO}_2$ where the five phases αFe , FeO , Fe_3O_4 , C and CO_2 are in equilibrium. By elimination of P_{CO_2} , P_{CO} and T from the above equations we find the coordinates of this point: $t = 571^\circ\text{C}$, $P = 0.0640\text{atm}$, $48.71\%\text{C}$.

In this 5-phase-point in total five 4-phase-lines intersect, each one appearing when one of the five phases is omitted. Beside the three lines mentioned above these are the lines $\alpha\text{Fe}-\text{FeO}-\text{Fe}_3\text{O}_4-\text{C}$ and $\alpha\text{Fe}-\text{FeO}-\text{Fe}_3\text{O}_4-\text{CO}_2$. The former line goes up from the 5-phase-point at constant temperature (and gas composition) to higher pressure, the latter line goes to lower temperature and pressure, at constant gas composition: Fig. 7a lines U and T , respectively.

THE 5-PHASE-POINT $\alpha\text{Fe}-\gamma\text{Fe}-\text{FeO}-\text{C}-\text{CO}_2$

At 733°C αFe and graphite form mixed-crystals of γFe . We may add FeO and a CO_2 mixture of the proper redox potential. If we next adjust the pressure to the value in equilibrium with graphite at this temperature we have the five phases αFe , γFe , FeO , C and CO_2 in equilibrium with one another at a 5-phase-point. This point lies on the 4-phase-line $\alpha\text{Fe}-\text{FeO}-\text{C}-\text{CO}_2$ which we calculated already above. This gives us, with the known temperature (733°C), gas composition and pressure: $t = 733^\circ\text{C}$, $P = 1.57\text{atm}$, $z = 60.83\%\text{CO}$.

The line $\alpha\text{Fe}-\text{Fe}-\text{C}-\text{CO}_2$ runs at a constant temperature of 733°C to lower pressures (Table H). $\alpha\text{Fe}-\gamma\text{Fe}-\text{FeO}-\text{C}$ runs at constant temperature to higher pressure. Calculation of the line $\gamma\text{Fe}-\text{FeO}-\text{C}-\text{CO}_2$ will follow after the line $\gamma\text{Fe}-\text{FeO}-\text{Fe}_3\text{O}_4-\text{C}-\text{CO}_2$. We measured part of the line $\alpha\text{Fe}-\gamma\text{Fe}-\text{FeO}-\text{CO}_2$. However, this line can be calculated also in another way. Clapeyron's equation for a mono-variant system reads $T dp/dT = Q/(V_1 - V_{12})$, where Q equals the heat of reaction between

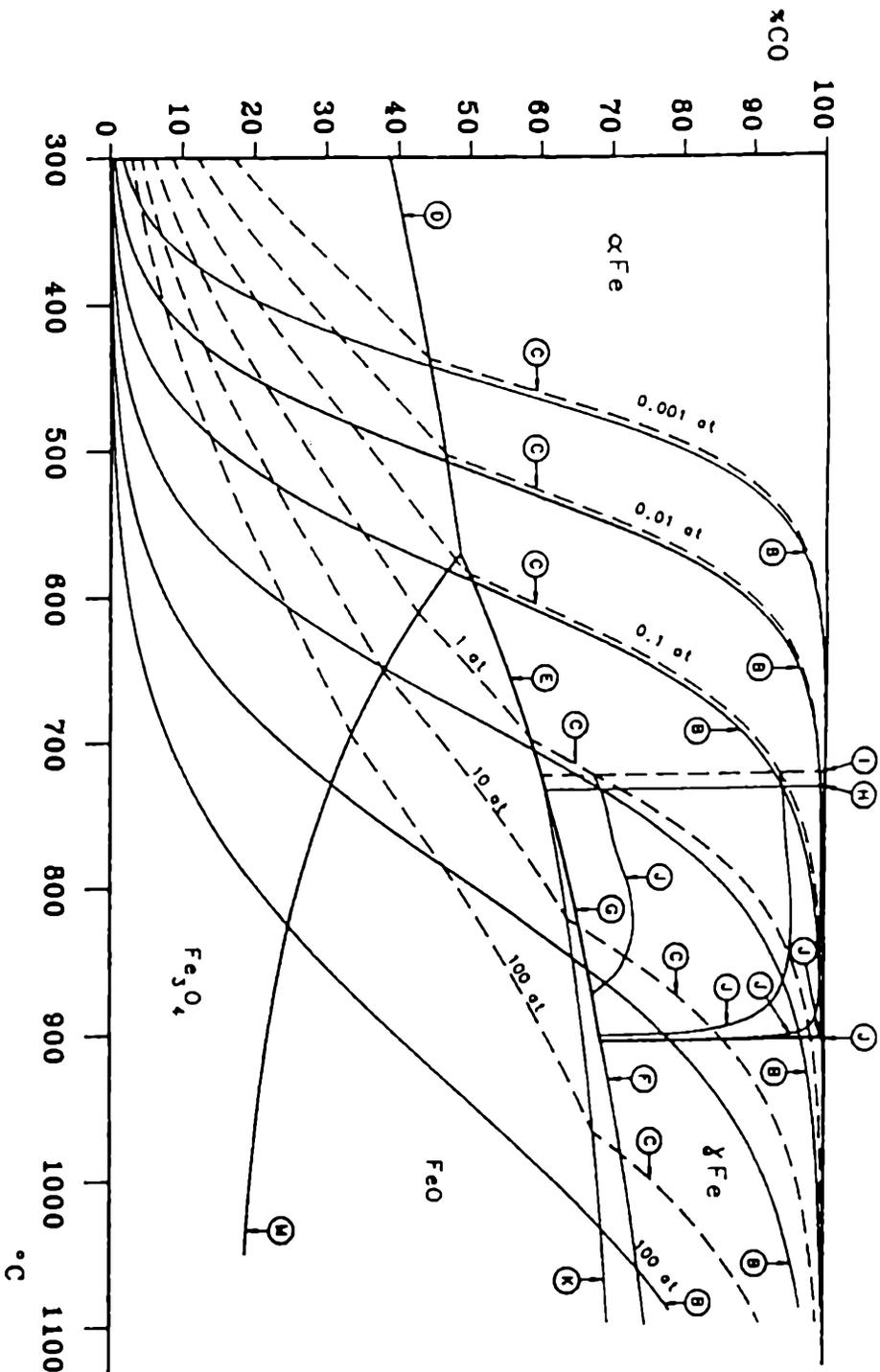


Fig. 5. Projection of the system Fe-C-O onto the T, z plane with cross-sections at pressures $P = 10^{-n}$, $n = -3, -2, -1, 0, 1$ and 2. Full lines: equilibria with graphite, dotted lines: equilibria with cementite

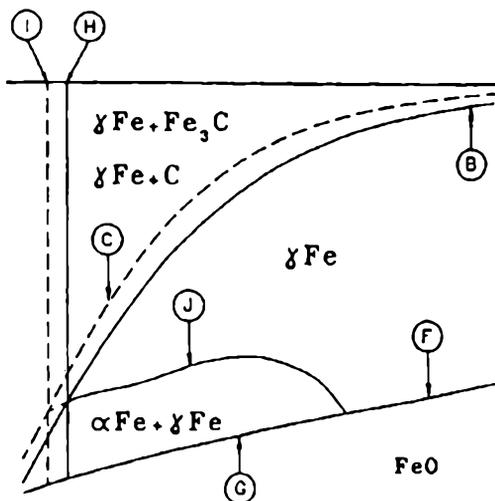
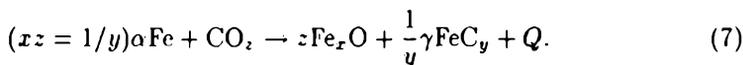


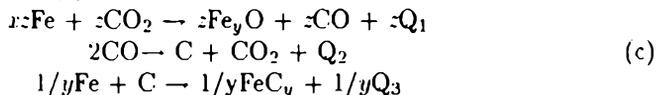
Fig. 6. Detail of Fig. 5 at $P = 1$ atm. The region between the 100% CO — coordinate and the lines H and B: 2-phase-area Fe + C; between the lines I and C: 2-phase-area Fe + Fe₃C; between J and F: 2-phase-area α Fe and γ Fe. The intermediate region: homogeneous γ Fe

the four phases α Fe, γ Fe, FeO and CO₂. These compounds react according to the reaction equation



In this equation the composition of Fe_xO is such that it is in equilibrium with α Fe. FeC_y is γ Fe in equilibrium with α Fe.

To calculate Q we split (7) into partial reactions:



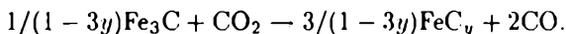
where $(z - 1)\text{CO}_2 + (2 - z)\text{CO}$ is exactly the composition CO₂ of the gas phase. z is given in Table F. Q_1 and Q_2 we found as ΔH of the respective reactions. Q_3 and y are taken from literature [7]. If we assume the gases ideal at these low pressures and neglect the volume V_2 of the solid phases, we have $dP/P = Q(T)/RT - dT$.

This equation can be integrated numerically. At 906°C the curve should reach the plane $P = 0$ which is a check on the accuracy.

There is still another method to calculate this line: If graphite dissolves in Fe to a concentration c , we have for the gas phase CO₂ in equilibrium with this solid phase $c_0 P_{\text{CO}_2}/P_{\text{CO}_2} = cK(T)$, where $c_0 = c_0(T)$ is the saturation of graphite in γ Fe and $K(T)$ the equilibrium constant of reaction (c). The solubility curves of α Fe and C in γ Fe give $P_{\text{CO}}/P_{\text{CO}_2}$ as a function of temperature. Also the ratio $P_{\text{CO}}/P_{\text{CO}_2}$ is known, thus we can calculate $P(T)$ for the line α Fe-Fe-FeO-CO₂. In Fig. 7 we show both lines together with a few measurements. The calculation of the line γ Fe-FeO-C-CO₂ will follow after the line γ Fe-FeO-Fe₃C-CO₂.

THE META-STABLE DIAGRAM

When cooling a solution of carbon in iron cementite (Fe_3C) may arise and with this compound (metastable) equilibria correspond. As mentioned already above we could not obtain cementite of sufficient purity. Therefore we took some data from the abounding literature. In exactly the same way as before we can find, from solubility curves of graphite and of cementite if γFe , the equilibrium constant of the reaction



We get $K = y_{cem}/y_{gra}K_B$ which this leads to

$$\log K = -8984/T + 9.403 - 8.68A + 11.85B + 3.153C. \quad (8)$$

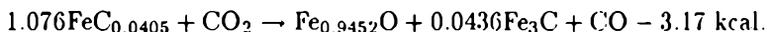
This gives a heat of formation of -4.61 kcal/mol and an entropy of formation of -5.24 cal/mol degree for the reaction of αFe and graphite producing cementite at 733°C . With this value we may calculate the meta-stable system.

At 723°C we have the 5-phase-point $\alpha\text{Fe}-\gamma\text{Fe}-\text{FeO}-\text{Fe}_3\text{C}-\text{CO}_2$. The gas composition we find from Tables E and F, the pressure from (8): $t = 723^\circ\text{C}$, $P = 1.54\text{atm}$, $60.24\%\text{C}$.

In an exactly similar way as above, we find the corresponding equilibria: in the first place the 5-phase-point $\alpha\text{Fe}-\text{FeO}-\text{Fe}_3\text{O}_4-\text{C}-\text{CO}_2$. As it contains the three phases αFe , FeO and Fe_3O_4 , it has the same temperature and gas composition as $\alpha\text{Fe}-\text{FeO}-\text{Fe}_3\text{O}_4-\text{C}-\text{CO}_2$, but a different pressure again given by (8). So we find for the coordinates of this point: $t = 571^\circ\text{C}$, $P = 0.073\text{atm}$, $48.71\%\text{CO}$. The results are given in the Tables. Finally, the line $\gamma\text{Fe}-\text{FeO}-\text{Fe}_3\text{C}-\text{CO}_2$. Below 723°C along the line $\alpha\text{Fe}-\text{FeO}-\text{Fe}_3\text{C}-\text{CO}_2$ the following reaction takes place:



At 723°C αFe reacts with Fe_3C to form γFe with a heat of reaction of 22 cal/g of perlite (eutectic mixture of $95.59\%\text{Fe} + 4.41\%\text{Fe}_3\text{C}$). So we find at 723°C for the reaction



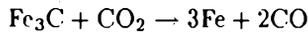
The differential heat of solution we calculate from the slope of the solubility curve of Fe_3C in γFe . Thus we find the values of Table L.

We now can calculate the line $\gamma\text{Fe}-\text{FeO}-\text{C}-\text{CO}_2$ which we postponed above. The reason is that the heat of dissociation of γFe into αFe and Fe_3C is better known than that of γFe into αFe and C . In quite the same way we find

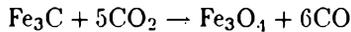
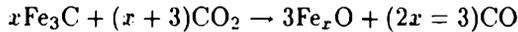
$$\log K = -625/T + 0.216 \log T + 0.130.$$

Also the other 4-phase-lines we find in an exactly analogous way as intersections of the corresponding 3-phase-planes, where we have to replace the plane $\text{C}-\text{CO}_2$ with

the plane indicating the equilibria of Fe_3C with CO_2 . This plane breaks into three parts as beside the reaction



there also exists the possibility of the reactions

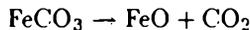


The results are given in the Tables.

EQUILIBRIA WITH FeCO_3 AS ONE OF THE PHASES

We performed our measurements of the dissociation of FeCO_3 over a too narrow temperature range as to allow extrapolation. As an equilibrium, if the specific heats of the compounds are known, is determined by two data, we still need one. From chemical data we can derive that formation of FeCO_3 from the elements under standard conditions ($t = 25^\circ\text{C}$, $P = 1$ atm) is accompanied with a change of thermodynamic potential $\Delta G = -161.030$ cal/mol.

This gives us for the reaction



$$\log P_{\text{CO}_2} = -3980/T + 8.224.$$

It is clear that this reaction does not lead to an equilibrium: in the first place because FeO is not a stable compound, but Fe_xO , and secondly, because ferrous oxide is oxidized by pure CO_2 . In the equilibrium state we have the phases FeCO_3 , Fe_3O_4 and CO_2 . The equilibrium constant of this equilibrium is given by

$$\log P_{\text{CO}} + 2 \log P_{\text{CO}_2} = -10.590/T + 23.171.$$

This plane intersects the C-CO_2 -plane giving the 4-phase-line FeCO_3 - Fe_3O_4 - C-CO_2 and the Fe_3CO_4 - Fe_2O_3 - CO_2 -plane along the line FeCO_3 - Fe_3O_4 - Fe_2O_3 - C-CO_2 . These 4-phase-lines given in the Table Q give no 5-phase-points below 100 atm.

THE LINE Fe_3O_4 - Fe_2O_3 - C-CO_2

Because Fe_2O_3 is reduced already by very small CO -concentrations we could not perform direct measurements of the equilibrium Fe_3O_4 - Fe_2O_3 - CO_2 . However, we can calculate the equilibrium constant. There exist some, very diverging, data of the oxygen pressure of Fe_2O_3 in equilibrium with Fe_3O_4 . Rather arbitrarily, we

take as an average $P_{O_2} = 1$ atm at 1450°C , together with a heat of formation of Fe_2O_3 of 195.200 ± 200 cal/mol. Then we have

$$\log P_{O_2} = -22.732/T + 13.193.$$

The dissociation constant of the reaction $2\text{CO}_2 \rightarrow 2\text{CO} + \text{O}_2$ is given by

$$\log P_{\text{CO}} + \log P_{O_2} - \log P_{\text{CO}_2} = -29.350/T - 9.32$$

and this leads to the expression for the equilibrium constant

$$\log P_{\text{CO}} - \log P_{\text{CO}_2} = -3309/T - 1.94 \quad \text{Table (N)}.$$

The intersection with the C-CO₂-plane gives the pressure of the 4-phase-line but this line lies far above 100 atm.

A NOVEL REPRESENTATION OF THE SYSTEM

The relation between temperature, pressure and gas composition in a ternary system leads to a 4-dimensional representation. Figs. 5 and 7 give the projections of this 4-dimensional space onto a T, z - and P, T -plane, respectively. Cross-sections at constant pressure produce prisms and cross-sections at constant temperature across these prisms make triangles. Fig. 8, e.g. gives a cross-section at 1 atm and 800°C . A point within this triangle Fe-C-O symbolizes a mixture in equilibrium, with gross composition indicated by the triangular coordinates of this point in the usual way. The triangle Fe-C-O is subdivided in small triangles and quadrangles. A point within a small triangle stands for an equilibrium mixture of three phases whose compositions are given by the three corners, in ratios again given by the triangular coordinates, unless two of the three corners represent gas phases. In the latter case only two phases appear, i.e. the one indicated by the third phase and the mixture of the gases. Any point within a quadrangle lies on a line whose ends indicate the two phases in equilibrium with one another.

We remark that in this triangle merely straight lines enter as long as no ternary phases with finite range enter. Now to any straight line in the plane a point can be attributed in a one-to-one relation. For example, if we write the equation of the line in the shape $x/a + y/b = 1$ there exists a one-to-one correspondence between this line and the point (a,b). We may, therefore, replace the lines in the triangle with points in a flat plane. If we change the temperature the lines move and the image points describe lines in the plane. The prism at constant pressure can be transformed into a plane figure where a temperature has been attributed to each point, so to a temperature field. If we put the pressure perpendicular to this plane we have a 3-dimensional representation of the Fe-C-O-system. The equilibria between αFe , FeO, Fe_3O_4 , Fe_2O_3 and CO_2 are pressure independent. As far as this part of the 4-dimensional representation concerns we may let the cross-sections at different pressure coincide. The equilibria between γFe , FeCO_3 , C, Fe_3C , and CO_2 are dependent of the pressure but it is simple to construct also for these equilibria a

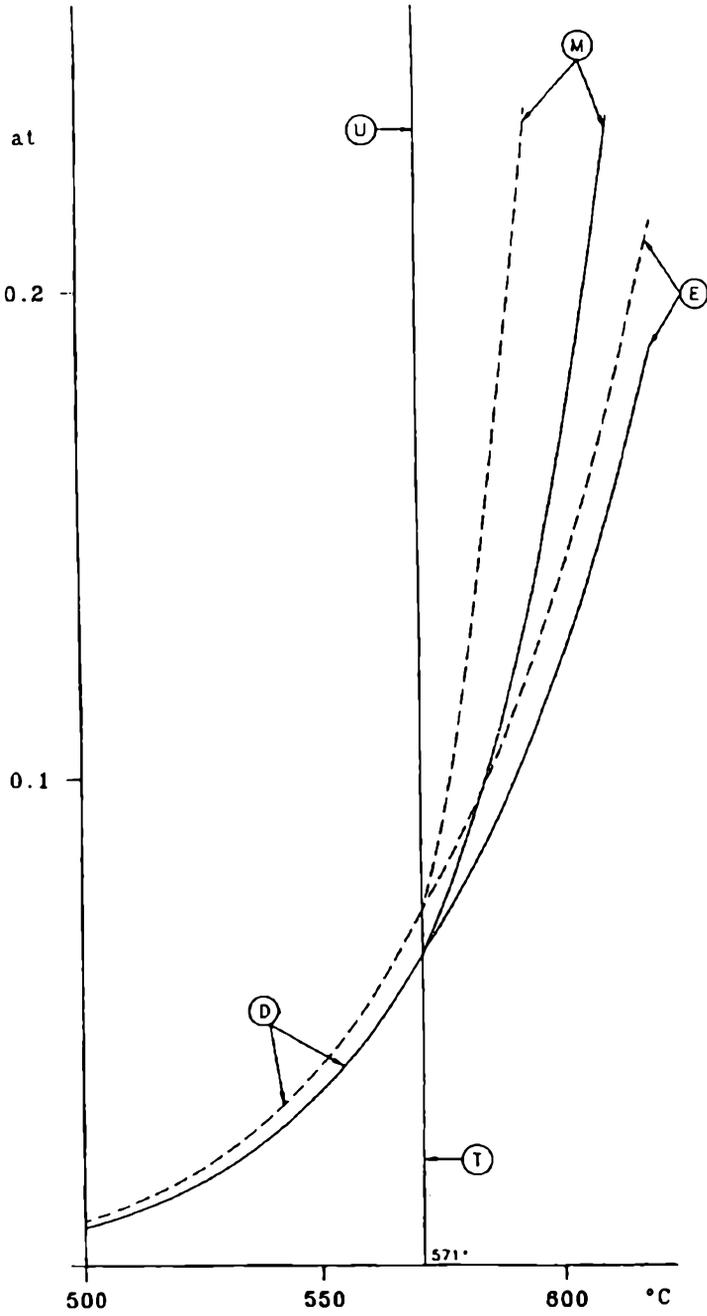


Fig. 7a. Cross-section around the quintuple points Fe, FeO, Fe₃O₄, (C resp. Fe₃C), CO₂

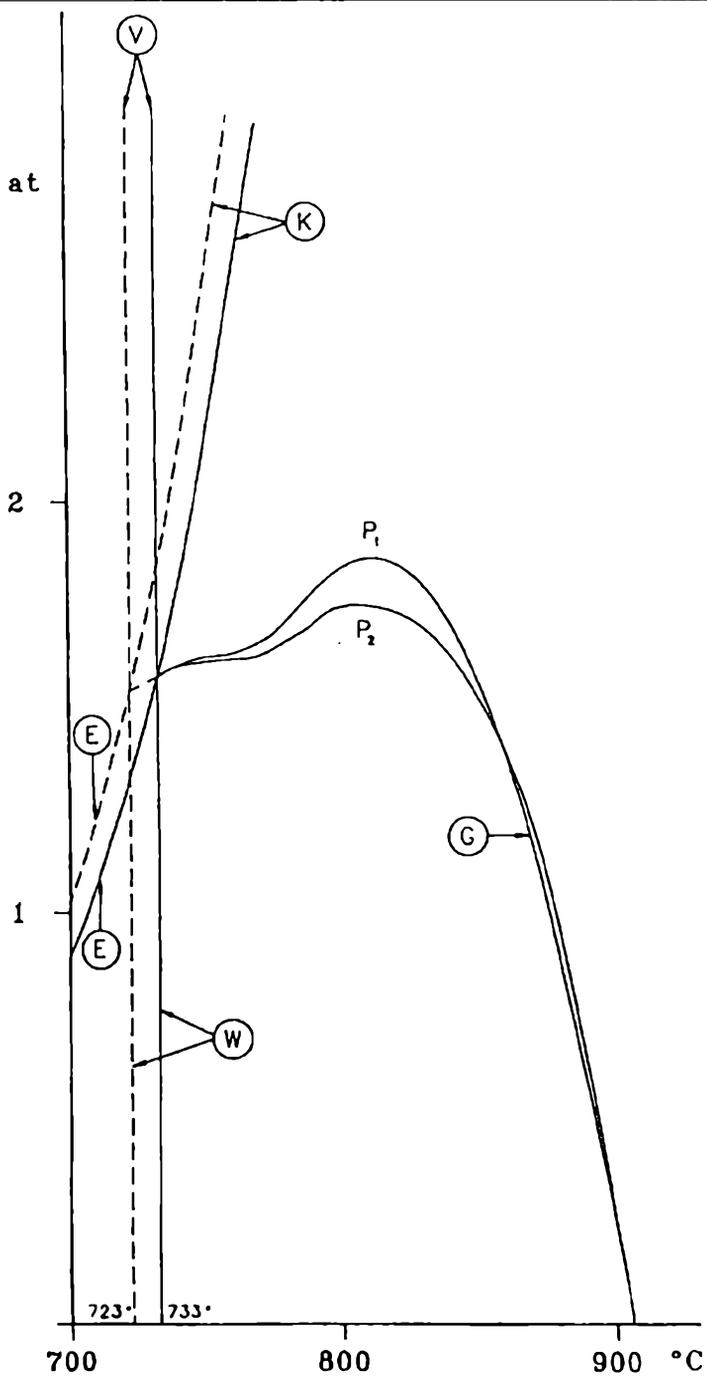


Fig. 7b. Cross-section around the quintuple points Fe, Fe, FeO, (C resp. Fe₃C), CO₂

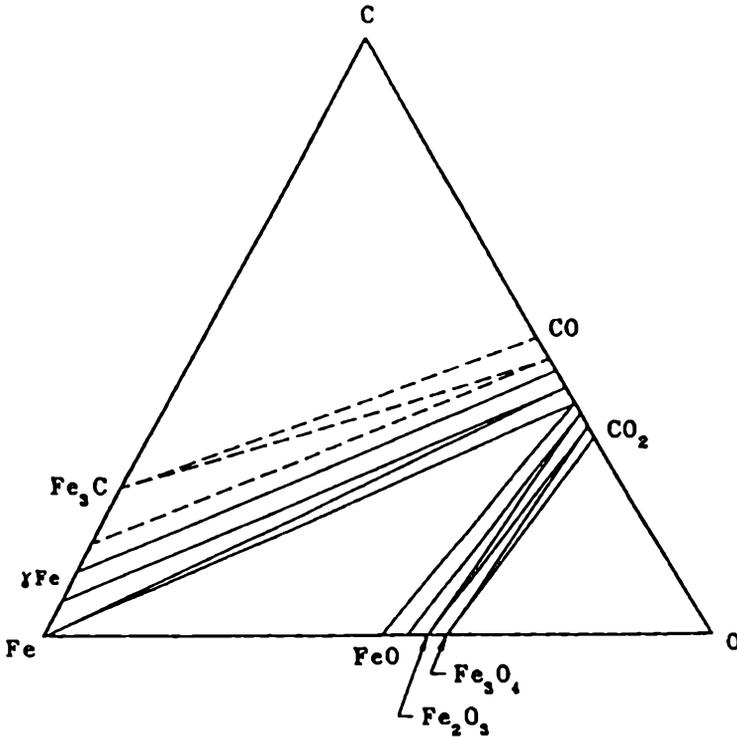


Fig. 8. Cross-section of the three-dimensional representation of the system Fe-C-O

2-dimensional Figure in which the relation between gas composition, temperature and pressure can be read: As it has been shown, the C-content in γFe , at a certain temperature and pressure, is proportional with the pressure, so c/P is independent of the pressure. This again can be represented in a 2-dimensional Figure.

All further equilibria can be written in the shape

$$n \log P_{\text{CO}} + m \log P_{\text{CO}_2} = f(T)$$

and also here a simple 2-dimensional representation can be constructed. The representation of the 4-dimensional space onto a 3-dimensional space is always possible in the way described above as long as no ternary phases appear with a finite range. When we mapped the 3-dimensional image in two dimensions we assumed the gas phase to obey the ideal gas law. Also without the latter supposition, however, a 2-dimensional representation is possible.

CONCLUSION

From a relatively small number of measurements and literature data we calculated the entire system of equilibria between iron, carbon and oxygen and their compounds in the temperature and pressure range 300–1100°C and 0–100 atm.

Though it may seem too optimistic when we assumed the ideal gas law to be valid up to 100 atm, gave the CO concentrations in two digits after the decimal point and the temperatures of the intersections of the isobars with the equilibrium lines with a precision of 1 degree, we believe the general structure of the Fe-C-O diagram to be right and complete: all measurements of equilibria should conform with this scheme.

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THE SYSTEM Fe-C-O

- A The five-phase points
- B The plane C-CO₂
- C The plane (α Fe, γ Fe, FeO or Fe₃O₃)-Fe₃C-CO₂
- D The lines α Fe-Fe₄O₄-(C or Fe₃C)-CO₂
- E The lines α Fe-FeO-(C or Fe₃C)-CO₂
- F The plane α Fe-FeO-CO₂
- G The line α Fe- γ Fe-FeO-CO₂
- H The line α Fe- γ Fe-C-CO₂
- I The line α Fe- γ Fe-Fe₃C-CO₂
- J The plane α Fe- γ Fe-CO₂
- K The line α Fe-FeO-C-CO₂
- L The line γ Fe-FeO-Fe₃C-CO₂
- M The lines FeO-Fe₃O₄-(C or Fe₃C)-CO₂
- N The plane Fe₃O₄-Fe₂O₃-CO₂
- O The dissociation pressure of FeCO₃ (not stable)
- P The dissociation of FeCO₃ in Fe₃O₄ and CO₂ (not stable)
- Q The line FeCO₃, α Fe, Fe₃O₄, CO₂
- R The dissociation pressure of Fe₂O₃ into Fe₃O₄ + O₂

Table A. The 5-phase-point

Phases					T	P	%CO
α Fe	FeO	Fe ₃ O ₄	C	CO ₂	571	0.064	48.71
α Fe	FeO	Fe ₃ O ₄	Fe ₃ C	CO ₂	571	0.073	48.71
α Fe	γ Fe	FeO	Fe ₃ C	CO ₂	723	1.54	60.24
α Fe	γ Fe	FeO	C	CO ₂	733	1.57	60.83

Table B. The 2-phase-plane C, CO₂

t	10 ⁻³	10 ⁻²	10 ⁻¹	1	10	100
300	1.63	0.52	0.16	0.25	0.02	0.01
350	6.78	2.20	0.70	0.22	0.07	0.02
400	21.44	7.36	2.39	0.76	0.24	0.08
450	49.73	19.86	6.77	2.19	0.70	0.22
500	79.71	42.45	16.20	5.44	1.75	0.56
550	94.39	69.53	32.69	11.83	3.91	1.25
600	98.54	88.29	54.83	22.69	7.83	2.55
650	99.58	96.12	75.86	38.34	14.29	4.76
700	99.87	98.69	89.31	56.79	23.84	8.27
750	99.95	99.52	95.61	73.84	36.40	13.43
800	99.98	99.81	98.17	85.98	50.88	20.48
850	99.99	99.92	99.20	92.95	65.24	29.40
900	100.00	99.96	99.62	96.48	77.35	39.86
950	100.00	99.98	99.81	98.19	86.11	51.09
1000	100.00	99.99	99.90	99.04	91.73	62.11
1050	100.00	99.99	99.95	99.46	95.10	71.95
1100	100.00	100.00	99.97	99.69	97.05	79.99

Table C. The equilibria (α -Fe, γ -Fe, FeO or Fe₃O₄), Fe₃C, CO₂

t	P	0.001	0.01	0.1	1	10	1000	at
300	Fe ₃ O ₄	17.03	12.16	8.57	5.97	4.14	2.85	Fe ₃ O ₄
350		26.26	19.29	13.87	9.82	6.87	4.77	
400		36.59	27.78	20.50	14.80	10.50	7.37	
450		52.95	36.94	28.08	20.74	14.98	10.64	
500	α -Fe	81.78	46.03	36.10	27.36	20.17	14.54	FeO
550		95.04	71.75	44.06	34.32	25.86	18.97	
600		98.71	89.43	57.03	41.27	31.83	23.80	
650		99.63	96.56	77.73	50.16	37.84	28.85	
700		99.88	98.86	90.46	59.19	46.16	34.00	
750		99.96	99.62	96.40	77.03	54.05	41.42	
800		99.99	99.87	98.68	89.22	61.16	48.42	
850	γ -Fe	99.99	99.95	99.49	95.32	72.74	54.95	FeO
900		100.00	99.98	99.79	97.97	84.82	60.86	
950		100.00	99.99	99.91	99.09	92.17	66.08	
1000		100.00	100.00	99.96	99.58	96.07	75.63	
1050		100.00	100.00	99.98	99.79	98.01	85.04	
1100	100.00	100.00	99.99	99.90	98.97	91.26		

Table D. The 4-phase-lines αFe , Fe_3O_4 , C or Fe_3C , CO_2

t	P(C)	P(Fe_3C)	%CO
300	1.10E-06	1.58E-06	38.73
350	1.75E-05	2.34E-05	40.85
400	1.82E-04	2.31E-04	42.85
436.6	8.17E-04	1.00E-03	44.22
450	1.36E-03	1.65E-03	44.71
500	7.77E-03	9.11E-03	46.45
503.0	8.57E-03	1.00E-02	46.55
550	3.57E-02	7.31E-02	48.71
571	6.40E-02	7.31E-02	48.71

Table E. The 4-phase-lines αFe , Fe_3O_4 , C or Fe_3C , CO_2

t	P(C)	P(Fe_3C)	%CO
571	0.0640	0.0731	48.71
584.8	0.0878	0.1000	49.96
600	0.1232	0.1401	51.30
650	0.348	0.396	55.31
698.8	0.870	1.000	58.72
700	0.889	1.023	58.80
723	1.329	1.541	60.24
733	1.574	.	60.83

Table F. The equilibrium Fe-FeO at P=0 571<t<906: αFe -FeO906<t: γFe -FeO

t	x
571	48.71
600	51.30
650	55.31
723	60.24
733	60.83
750	31.80
800	64.39
850	66.60
900	68.50
906	68.71
950	70.39
1000	72.10
1050	73.62
1100	74.98

Table G. The 4-phase-line αFe , γFe , FeO, CO_2

t	P_1	P_2
723	1.541	
733	1.574	1.575
740	1.602	1.600
750	1.623	1.612
770	1.660	1.627
780	1.712	1.663
790	1.740	1.704
800	1.839	1.746
820	1.851	1.735
840	1.707	1.633
860	1.383	1.391
880	0.872	0.949
900	0.238	0.260
906	0.000	0.000

Table H. 4-phase-line αFe , γFe , FeO, CO_2

t	x	P(C)
733	0.6083	1.574
733	0.65	1.232
733	0.70	0.910
733	0.75	0.661
733	0.80	0.465
733	0.85	0.309
733	0.90	0.184
733	0.95	0.082
733	1.00	0.000

Table I. 4-phase-line αFe , γFe , FeO, CO_2

t	x	P(Fe_3C)
723	0.60	1.541
723	0.65	1.165
723	0.70	0.861
723	0.75	0.625
723	0.80	0.439
723	0.85	0.292
723	0.90	0.174
723	0.95	0.078
723	1.00	0.000

Table J. The plane αFe , γFe , CO_2

t	0.001	0.01	0.1	1 atm
723	99.93	99.30	93.75	67.54
733	99.93	99.34	94.05	68.47
740	99.93	99.36	94.21	68.26
750	99.94	99.38	94.37	69.48
760	99.94	99.39	94.50	69.90
770	99.94	99.41	94.64	71.36
780	99.94	99.43	94.83	71.02
790	99.95	99.46	95.04	71.74
800	99.95	99.48	95.24	72.45
810	99.95	99.49	95.35	72.85
820	99.95	99.50	95.41	73.08
830	99.95	99.50	95.41	73.07
840	99.95	99.49	95.28	72.61
850	99.95	99.46	95.07	71.83
860	99.94	99.42	94.71	70.60
870	99.93	99.33	94.01	68.35
876	99.92	99.25	93.39	66.48
880	99.92	99.18	92.79	.
890	99.88	98.79	89.96	.
900	99.70	97.19	80.65	.
903.6	99.30	93.75	67.56	.
905.7	95.00	71.60	.	.
905.97	71.66	.	.	.

Tables K. (C) and L. (Fe_3C)

t	P(C)	P(Fe_3C)	$x(\text{C})$	$x(\text{Fe}_3\text{C})$
723	1.32	1.54	60.33	60.22
733	1.57	1.85	60.82	60.71
750	2.10	2.49	61.63	61.52
800	4.68	5.69	63.83	63.72
850	9.68	12.20	65.79	65.69
900	18.78	24.75	67.56	67.45
950	34.46	48.81	69.14	69.04
1000	60.18	88.51	70.56	70.47
1050	100.62	157.82	71.85	71.76
1100	161.78	.	73.03	72.93

Table M. The 4-phase-lines FeO , Fe_3O_4 , C or Fe_3C , CO_2

t	P(C)	P(Fe_3C)	x
571	0.0640	0.0731	48.71
575.6	0.0763	0.0998	47.99
600	0.188	0.489	44.40
611.6	0.282	1.000	42.83
650	1.016	9.405	38.10
651.1	1.053	9.995	37.98
695.3	3.990	100.1	33.51
700	4.560	126.0	33.39
750	17.35	.	29.17
800	57.1	.	26.12
850	165.1	.	23.78
900	.	.	21.98
950	.	.	20.62
1000	.	.	19.61
1050	.	.	18.89
1100	.	.	18.41

Table N. The plane Fe_3O_4 , Fe_2O_3 , CO_2

t C	P atm
600	1.88E-04
650	3.02E-04
700	4.61E-04
750	6.76E-04
800	9.56E-04
850	1.31E-03
900	1.75E-03
950	2.28E-03
1000	2.92E-03
1050	3.66E-03
1100	4.51E-03
1150	5.48E-03
1200	6.57E-03
1250	7.79E-03
1300	9.13E-03
1350	1.06E-02
1400	1.22E-02
1450	1.39E-02
1500	1.58E-02

Table R. O_2 -pressure of Fe_2OFe_3

t C	P atm
600	1.44E-13
650	3.70E-12
700	6.81E-11
750	9.43E-10
800	1.02E-08
850	8.97E-08
900	6.54E-07
950	4.05E-06
1000	2.17E-05
1050	1.03E-04
1100	4.43E-04
1150	1.66E-03
1200	5.77E-03
1250	1.85E-02
1300	5.52E-02
1350	1.54E-01
1400	4.03E-01
1450	1.00E+00
1500	2.36E+00

Table O. Dissociation of FeCO_3

t	P(CO_2)	%CO
100	0.00356	0.00
150	0.06396	0.00
200	0.6243	0.00
250	3.9628	0.00
300	18.36	0.00
350	67.19	0.00
400	205.02	0.00

Table P. Dissociation of FeCO_3 , Fe_3O_4 and CO_2

t	P(CO_2)	%CO
100	0.1029	33.33
150	0.9973	33.33
200	6.015	33.33
250	26.02	33.33
300	88.43	33.33
350	251.03	33.33

Table Q. The 4-phase-line FeCO_3 , αFe , Fe_3O_4 , CO_2

t	P(CO)	P(CO_2)	P	%CO
100	0.030	0.0733	0.103	29.05
150	0.316	0.6823	0.998	31.63
200	2.052	3.963	6.016	34.12
250	9.51	16.56	26.08	36.49
300	34.47	54.52	88.99	38.73
350	103.79	150.26	254.05	40.85

The field boundaries are indicated in Tables D, H or I, K and M.