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IM. STANISŁAWA STASZICA W KRAKOWIE
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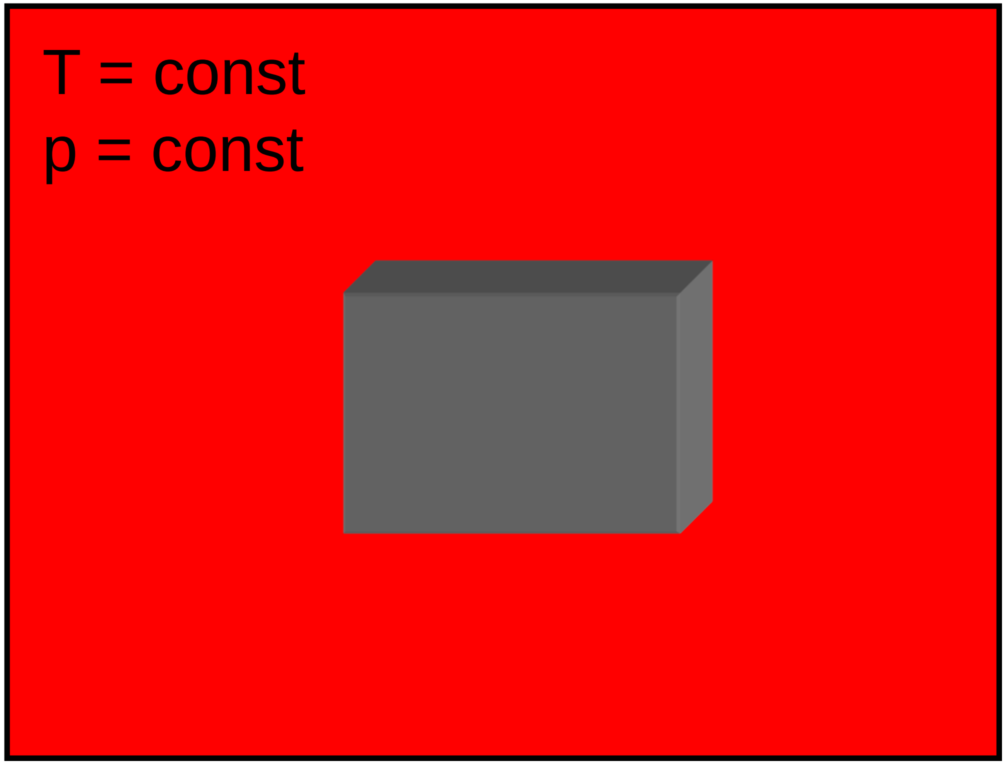
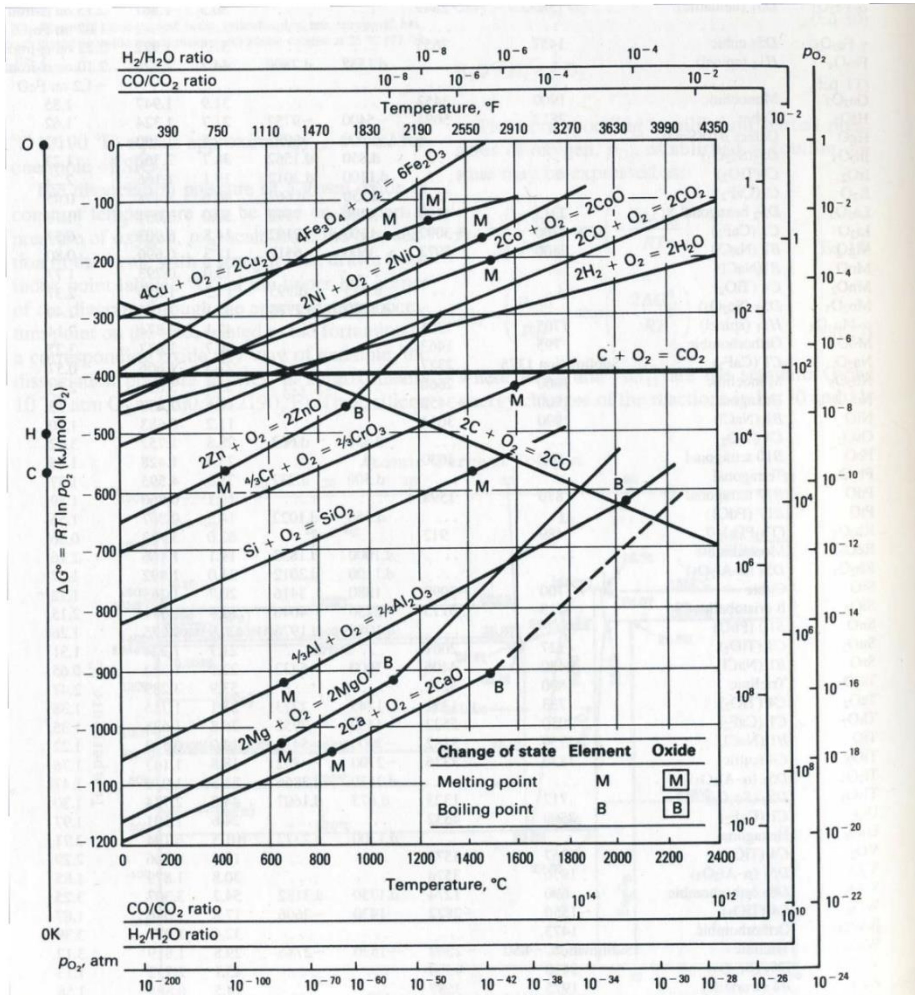
THERMODYNAMICS OF HIGH TEMPERATURE CORROSION PROCESSES

http://home.agh.edu.pl/~grzesik

Scheme of high temperature corrosion process



Ellingham-Richardson diagrams
(Richardson-Jeffes)



S. Mrowec, *An Introduction to the Theory of Metal Oxidation*, National Bureau of Standards and National Science Foundation, Washington D.C., 1982.

Ellingham-Richardson diagrams
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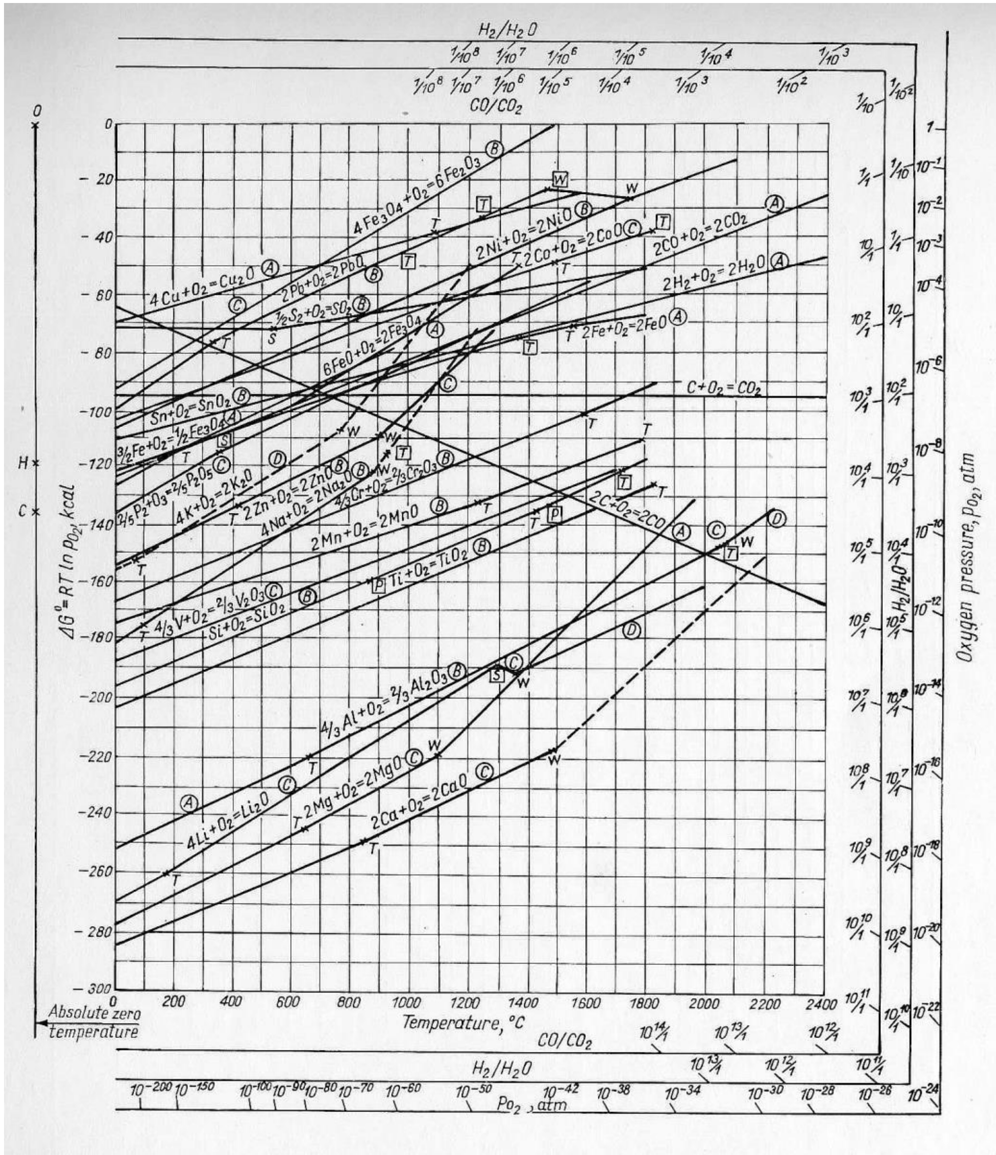

Ellingham-Richardson diagrams
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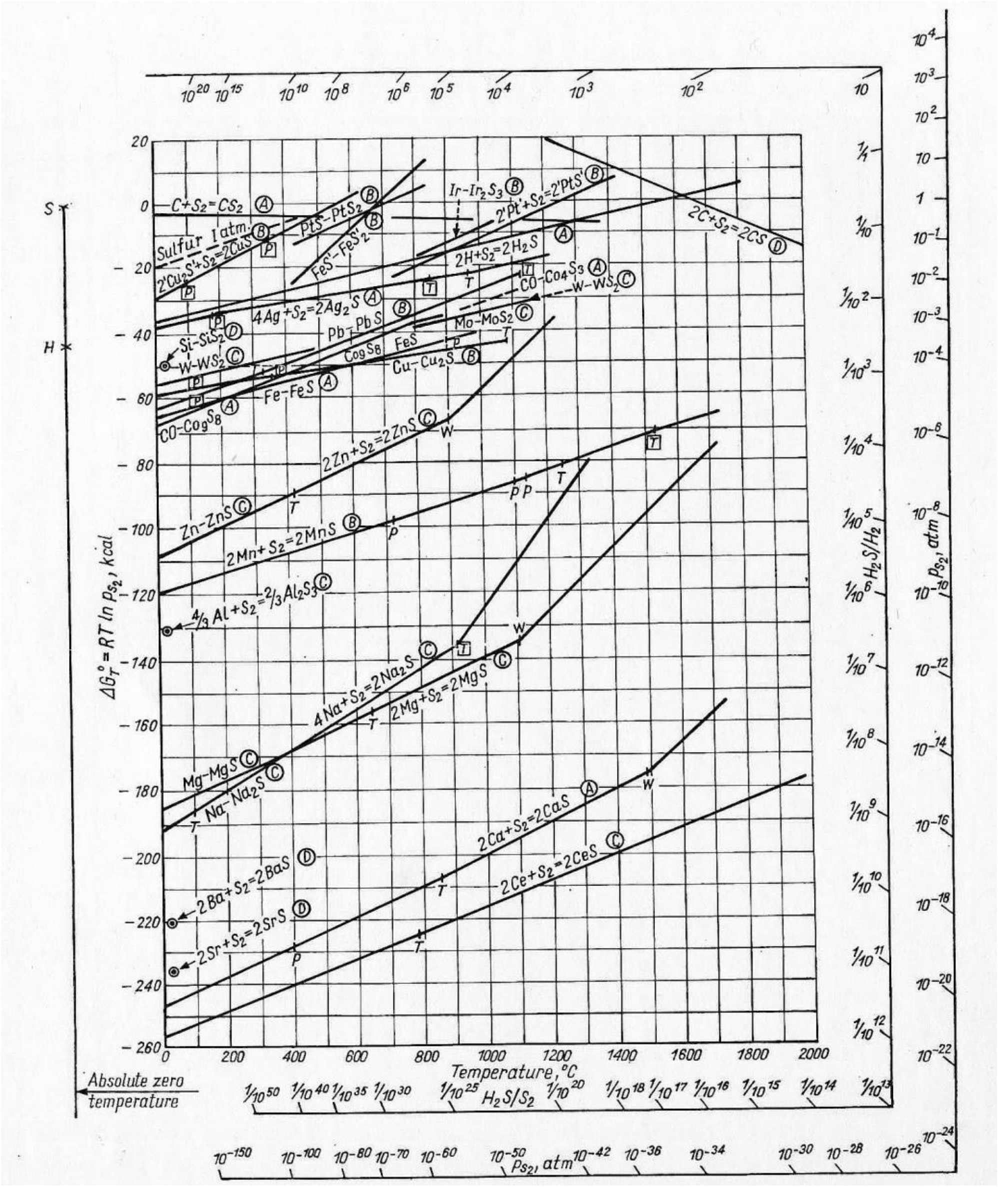

Ellingham-Richardson diagrams
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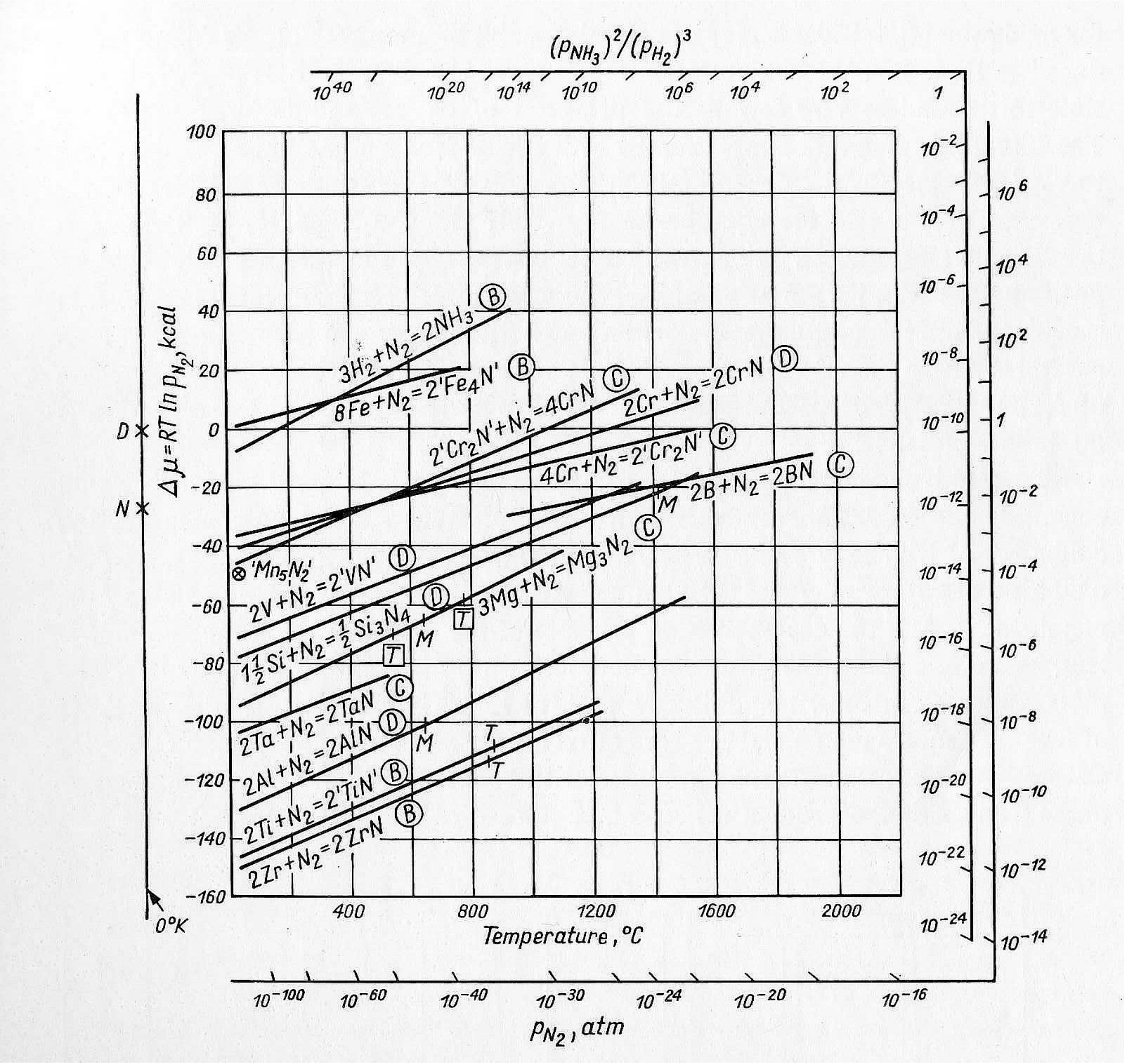
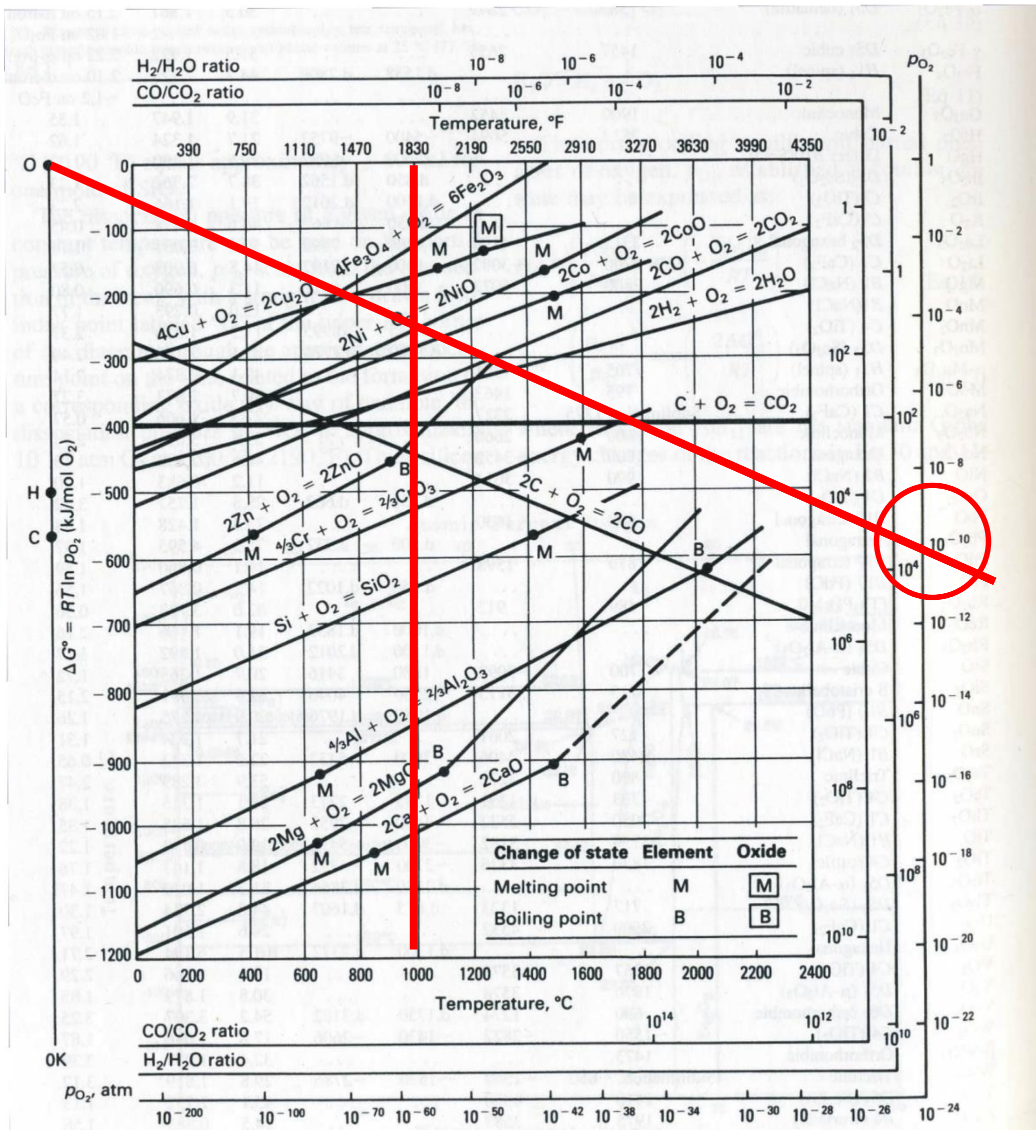


Determining dissociation pressures



Example:
determine the dissociation pressure of NiO at 1000 °C

answer: p (NiO) = 10^{-10} atm

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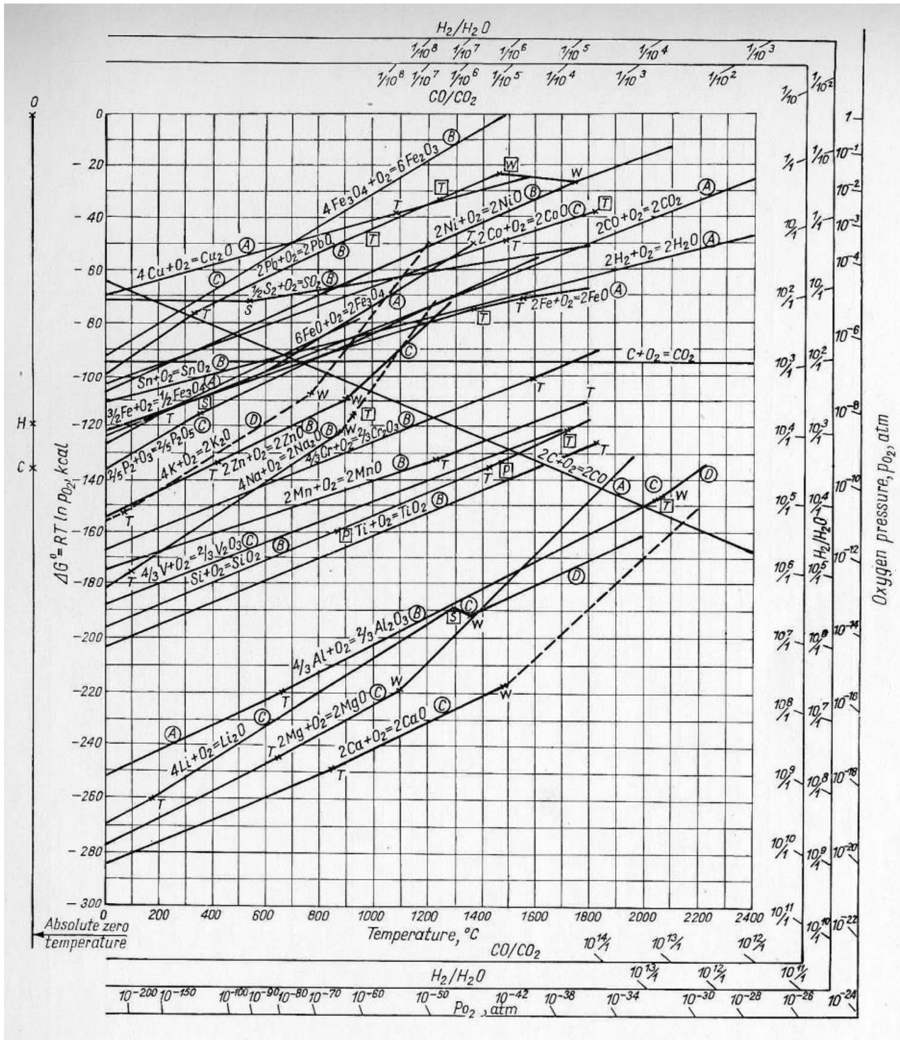
Sequence of oxides in a multiphase scale



Example:
determine the sequence of oxide formation in the scale grown on iron after oxidation in air at 1000 oC

answer:
$p(FeO) \approx 10^{-15}$ atm
$p(Fe_3O_4) \approx 10^{-12}$ atm
$p(Fe_2O_3) \approx 10^{-5}$ atm

$Fe/FeO/Fe_3O_4/Fe_2O_3/O_2$

Determining dissociation pressures

$$Me + \frac{1}{2} X_2 \Leftrightarrow MeX \quad (1)$$

where: Me – metal; X2 – oxidant;
MeX – product of oxidation reaction (scale)

$$\Delta G = \mu_{MeX} - \mu_{Me} - \frac{1}{2}\mu_{X_2}$$

where: ΔG – the free energy change of reaction (1)
μ_i – the chemical potential of a given component

$$\mu_i = \mu_i^0 + RT \ln a_i$$

where:
R – universal gas constant
T – temperature [K]
a_i – activity of i - component in the system
μ_i^0 – standard chemical potential of i - component (i.e. when its activity is equal to 1)

Determining dissociation pressures, cont.

In the case of pure substances in the solid phase:

$$\mu_{Me} = \mu_{Me}^{0} \qquad \mu_{MeX} = \mu_{MeX}^{0}$$

In the case of substances in the gas phase:

$$\mu_{X_2} = \mu_{X_2}^{0} + RT\ln a_{X_2} = \mu_{X_2}^{0} + RT\ln p_{X_2}$$

$$\Delta G = \mu_{MeX} - \mu_{Me} - \tfrac{1}{2}\mu_{X_2} = \mu_{MeX}^{0} - \mu_{Me}^{0} - \tfrac{1}{2}\mu_{X_2}^{0} - \tfrac{1}{2}RT\ln p_{X_2} = \Delta G^{0} - \tfrac{1}{2}RT\ln p_{X_2}$$

At thermodynamic equilibrium $\Delta G = 0$:

$$p_{X_2} = \exp\left(\frac{2\cdot\Delta G^{0}}{RT}\right)$$

Sequence of oxides in a multiphase scale

Example: determine the sequence of oxide formation in the scale grown on iron oxidized in air at 1000 ^{o}C

$$Fe + \tfrac{1}{2}O_2 = FeO \qquad p(FeO) = 2.7\cdot 10^{-16}\ \text{atm}$$

$$3Fe + 2O_2 = Fe_3O_4 \qquad p(Fe_3O_4) = 3.1\cdot 10^{-15}\ \text{atm}$$

$$2Fe + \tfrac{3}{2}O_2 = Fe_2O_3 \qquad p(Fe_2O_3) = 3.0\cdot 10^{-14}\ \text{atm}$$

$$3FeO + \tfrac{1}{2}O_2 = Fe_3O_4 \qquad p(Fe_3O_4) = 4.6\cdot 10^{-12}\ \text{atm}$$

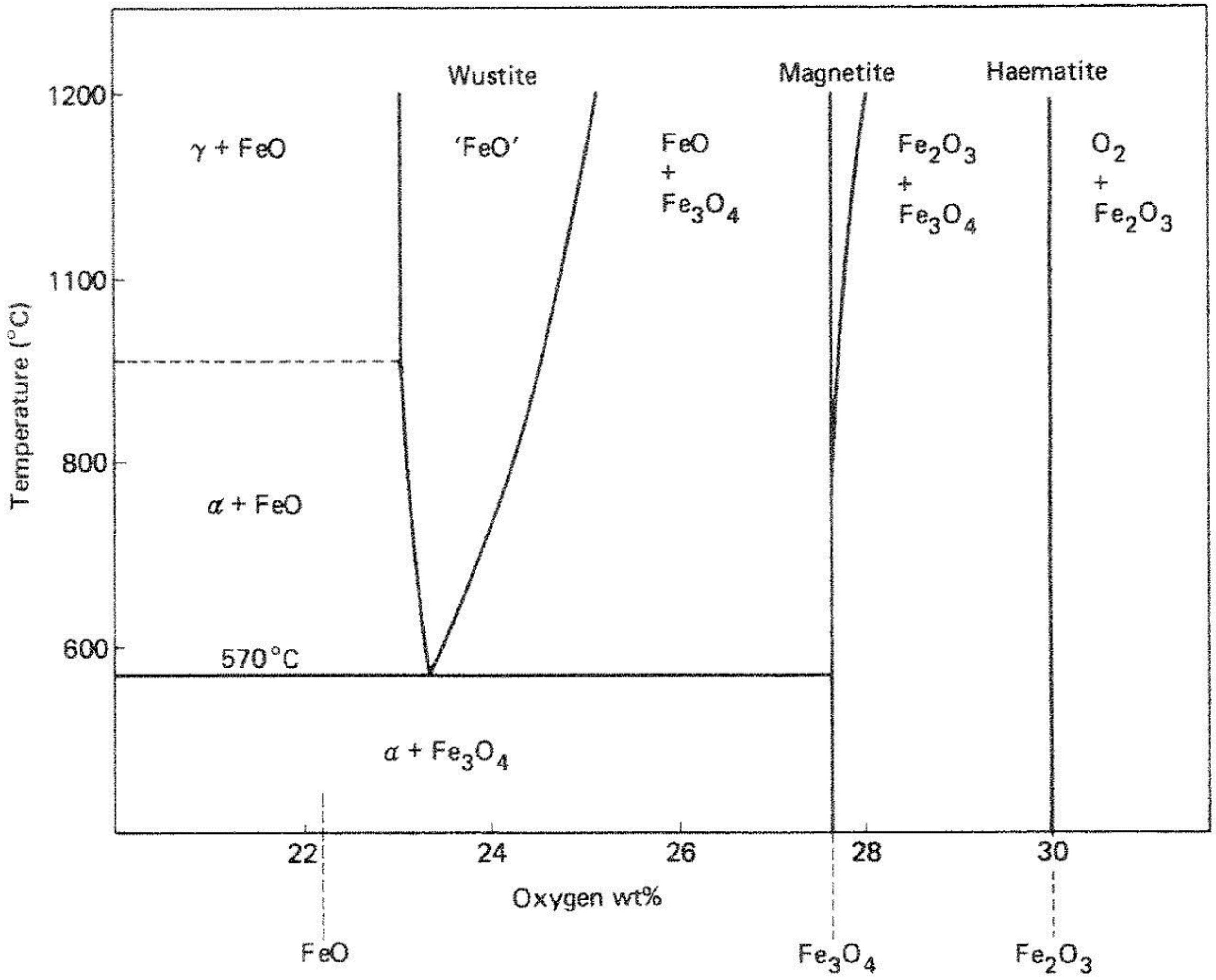
$$2FeO + \tfrac{1}{2}O_2 = Fe_2O_3 \qquad p(Fe_2O_3) = 3.7\cdot 10^{-10}\ \text{atm}$$

$$2Fe_3O_4 + \tfrac{1}{2}O_2 = 3Fe_2O_3 \qquad p(Fe_2O_3) = 2.4\cdot 10^{-6}\ \text{atm}$$

$$Fe/FeO/Fe_3O_4/Fe_2O_3/O_2$$

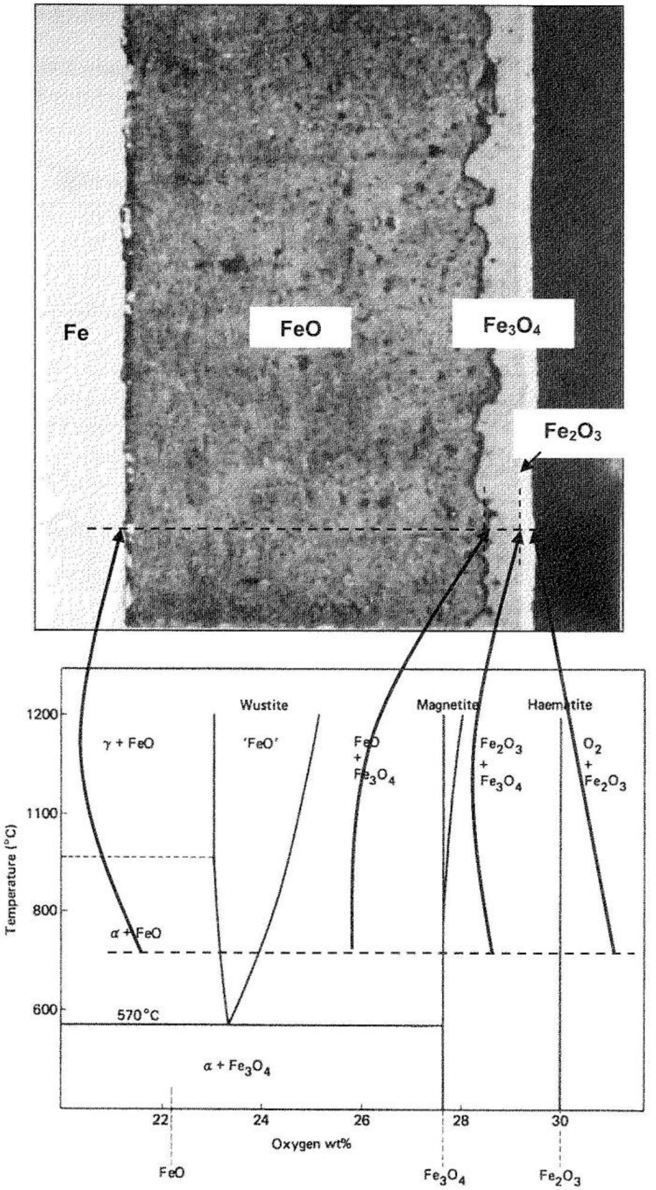
Z. Grzesik, "Thermodynamics of gaseous corrosion" in ASM Handbook, vol. 13a, p.90-96, ASM International, Materials Park, Ohio, USA, 2003.

Phase diagram of the Fe-O system



David J. Young, „High temperature oxidation and corrosion of metals", Elsevier, Sydney 2016.

Cross-section of the oxide scale growing on iron in accordance with the Fe-O phase diagram



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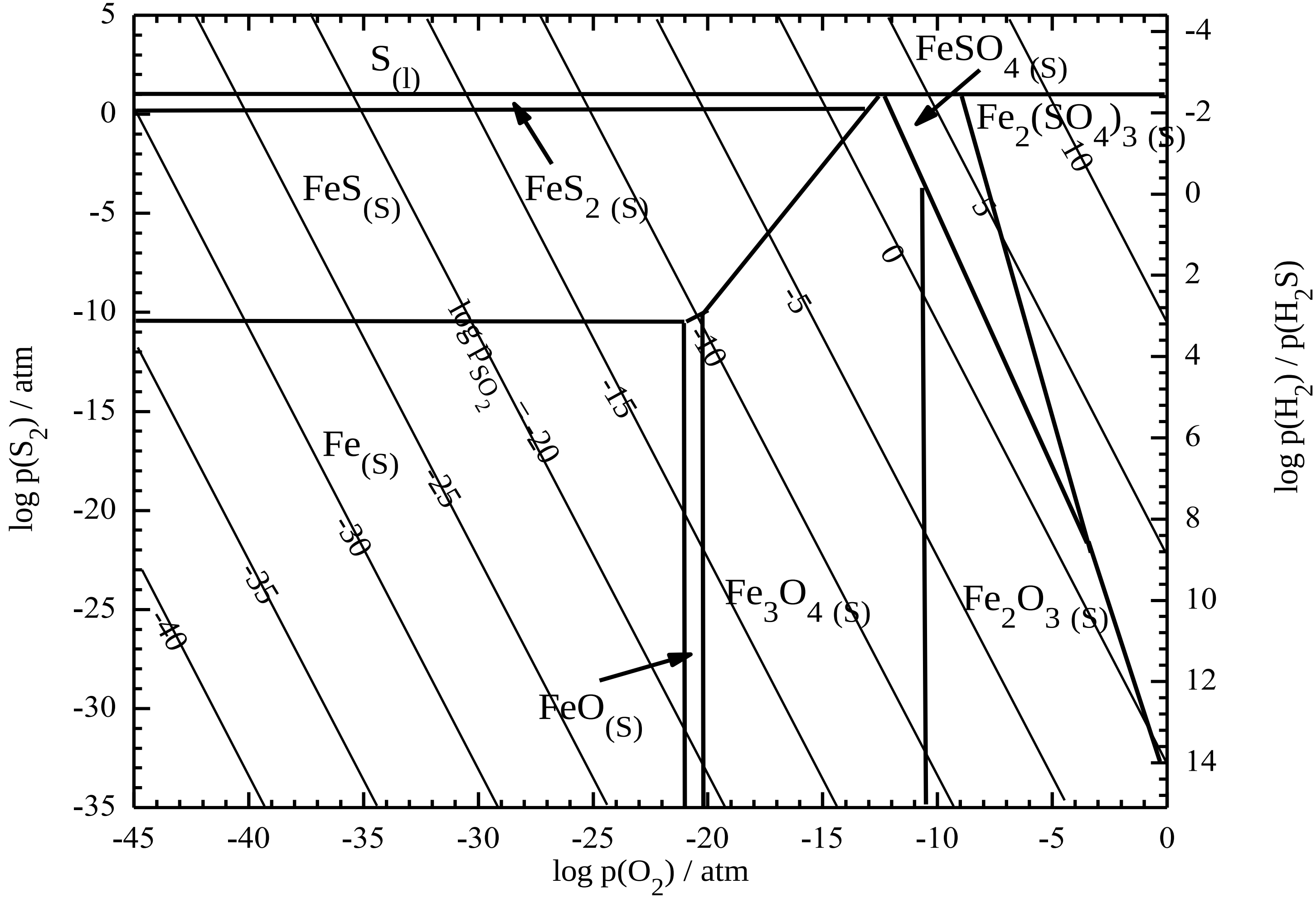
Kellogg diagrams



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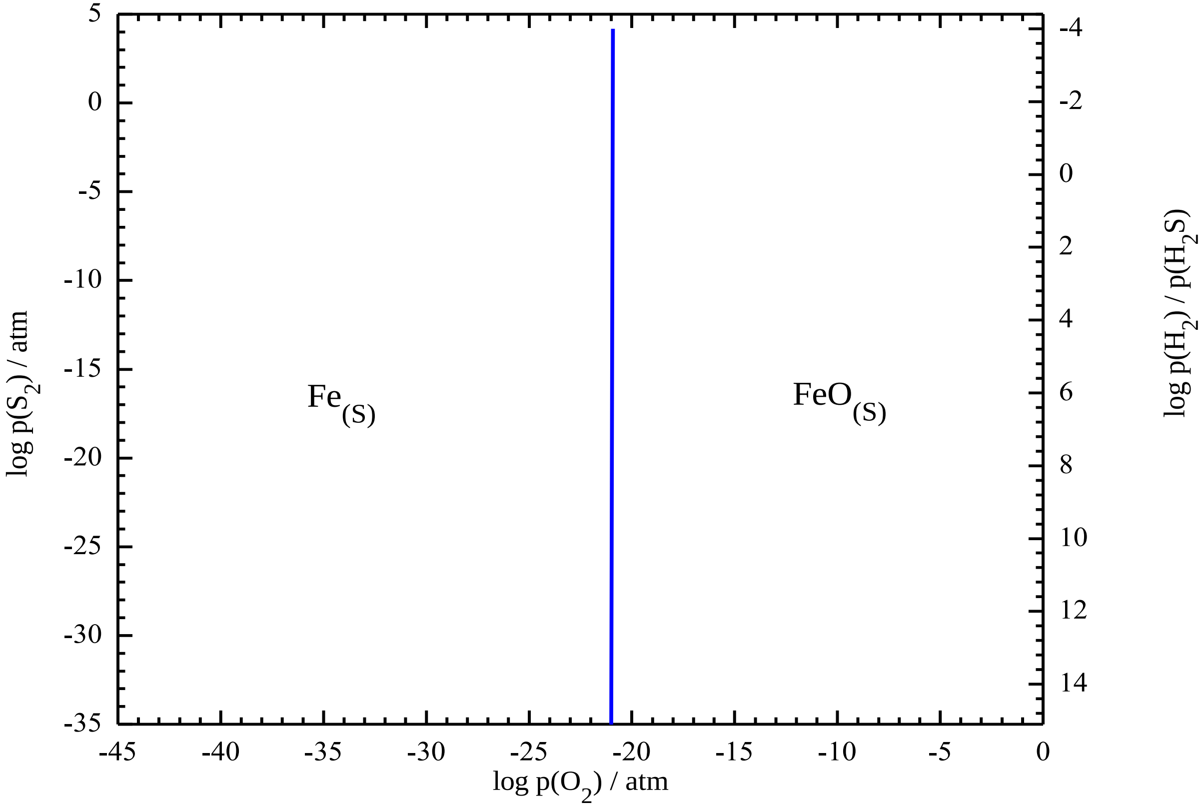
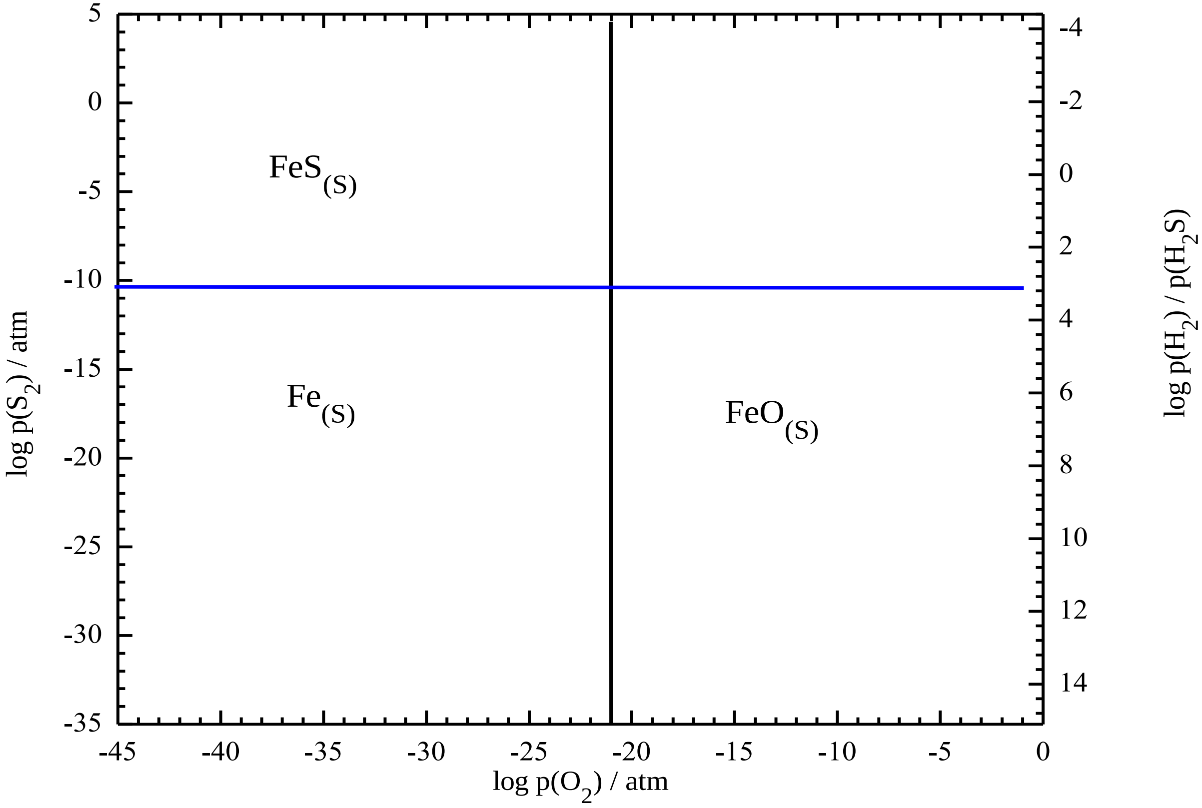
Kellogg diagrams



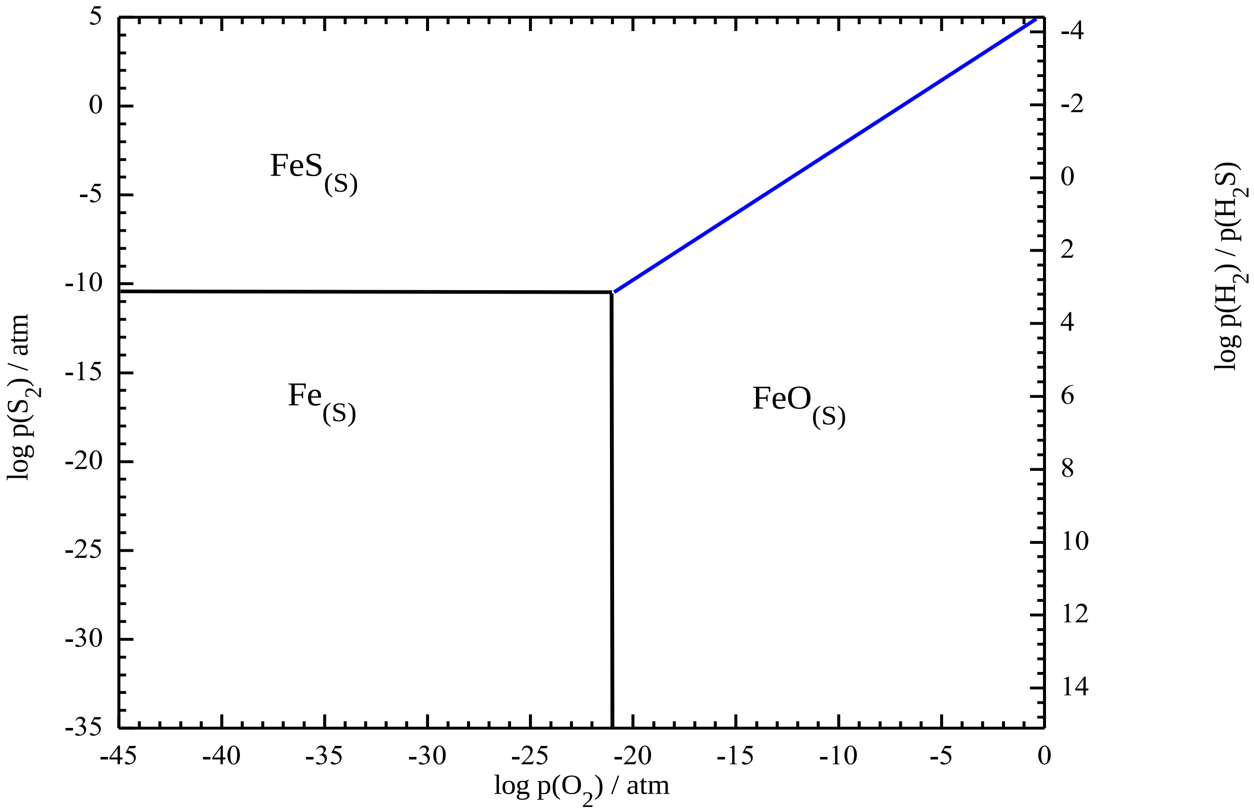
$$Fe + \tfrac{1}{2}O_2 \Leftrightarrow FeO$$

Kellogg diagrams



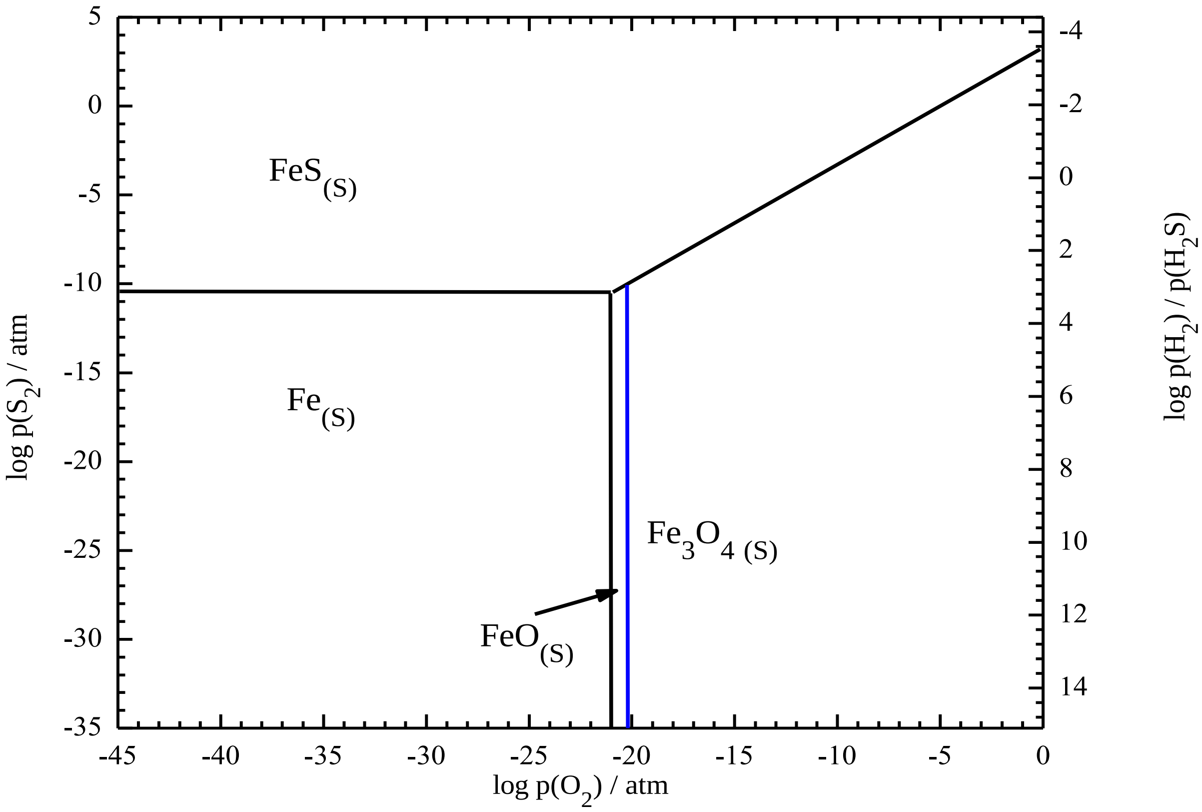
$$Fe + \frac{1}{2}S_2 \Leftrightarrow FeS$$

Kellogg diagrams



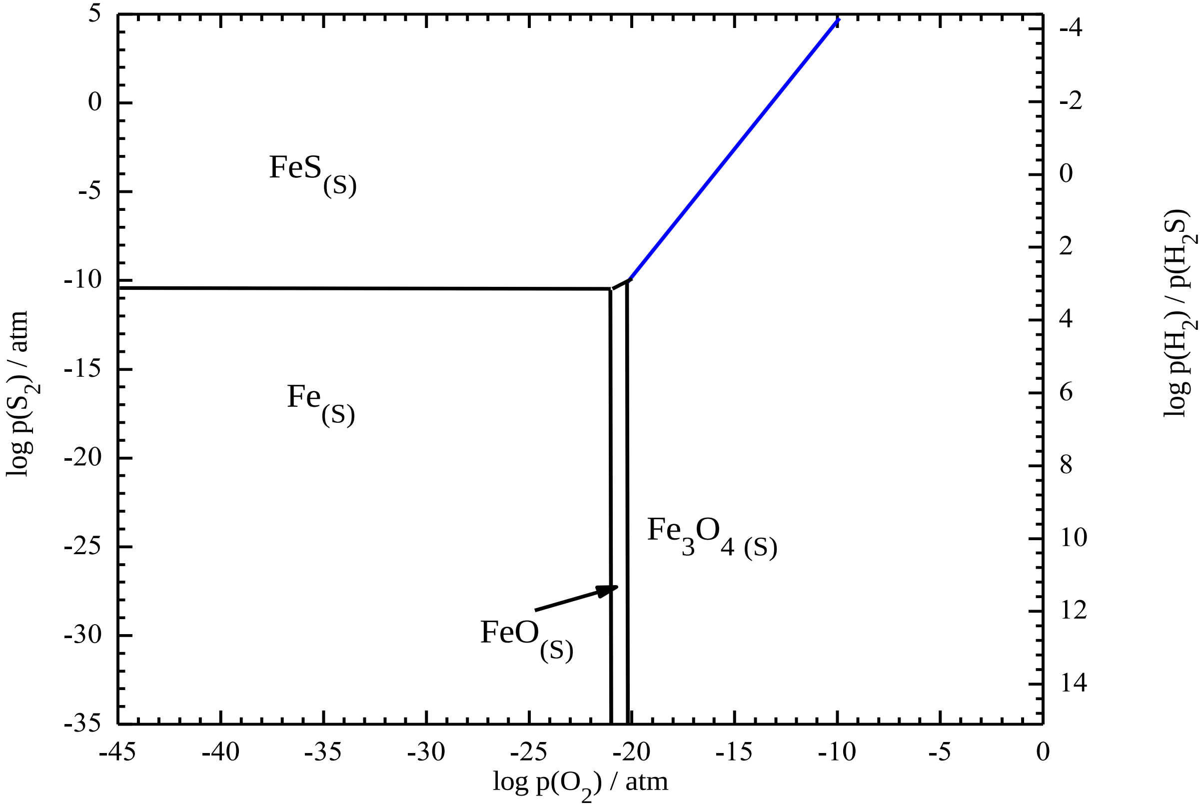
$$FeO + \tfrac{1}{2}S_2 \Leftrightarrow FeS + \tfrac{1}{2}O_2$$

Kellogg diagrams



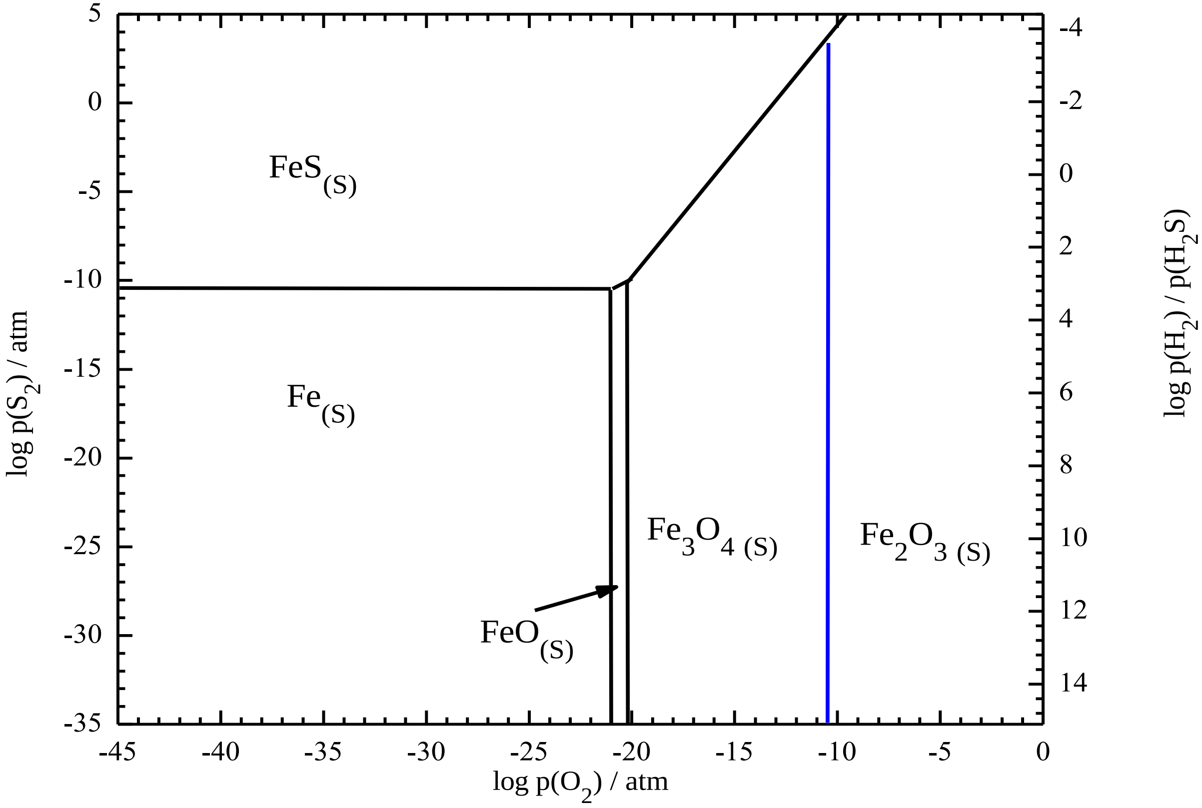
$$3FeO + \tfrac{1}{2}O_2 \Leftrightarrow Fe_3O_4$$

Kellogg diagrams



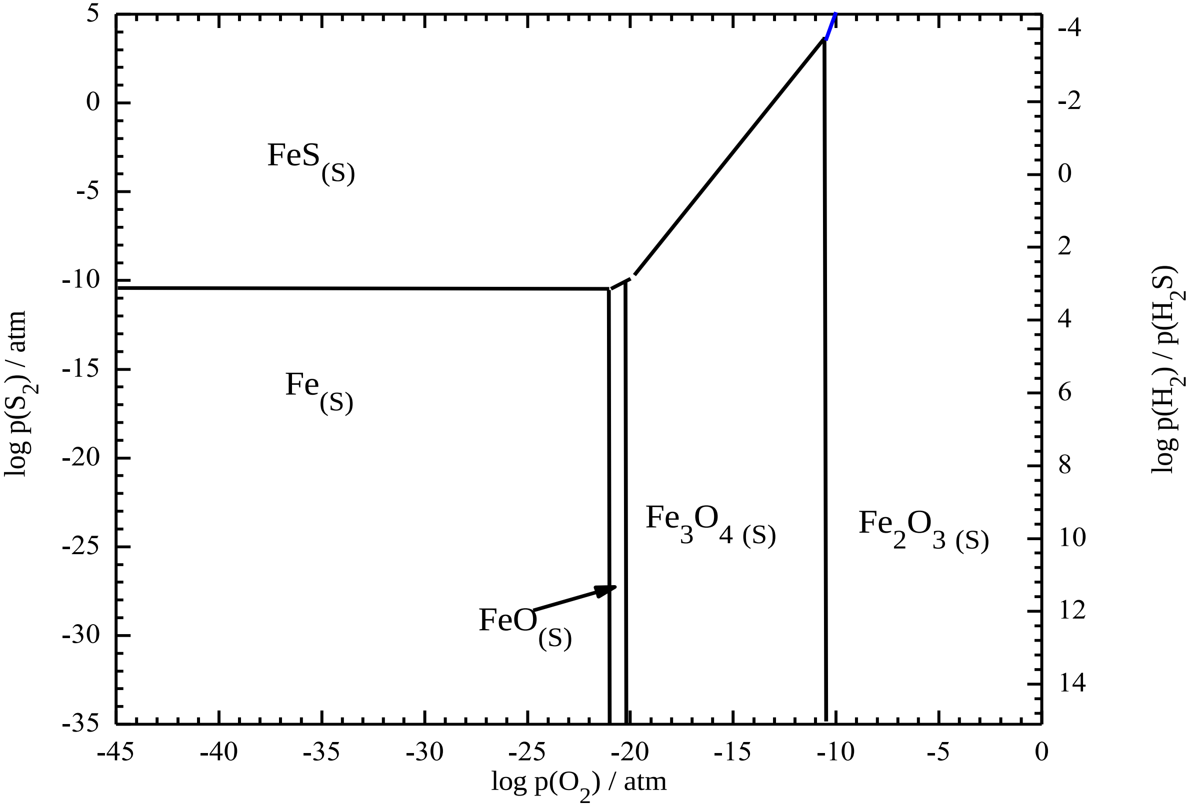
$$Fe_3O_4 + \frac{3}{2}S_2 \Leftrightarrow 3FeS + 2O_2$$

Kellogg diagrams



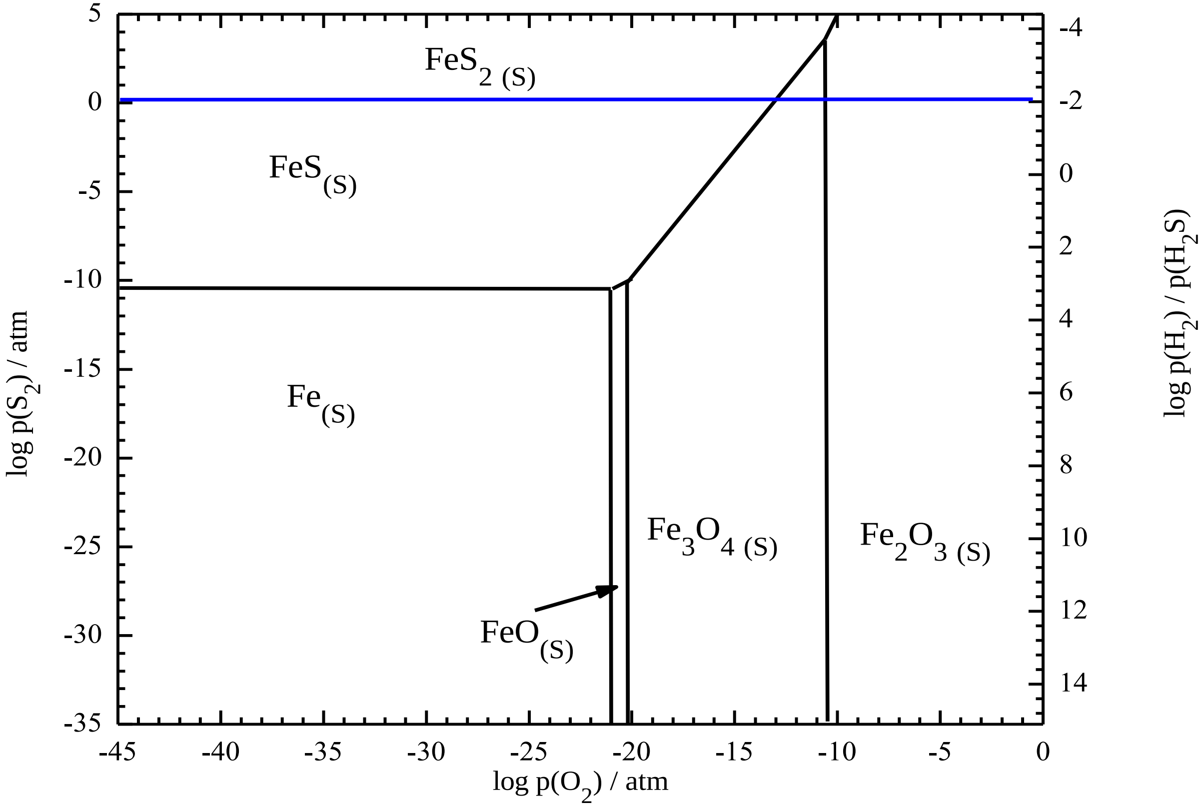
$$2Fe_3O_4 + \frac{1}{2}O_2 \Leftrightarrow 3Fe_2O_3$$

Kellogg diagrams



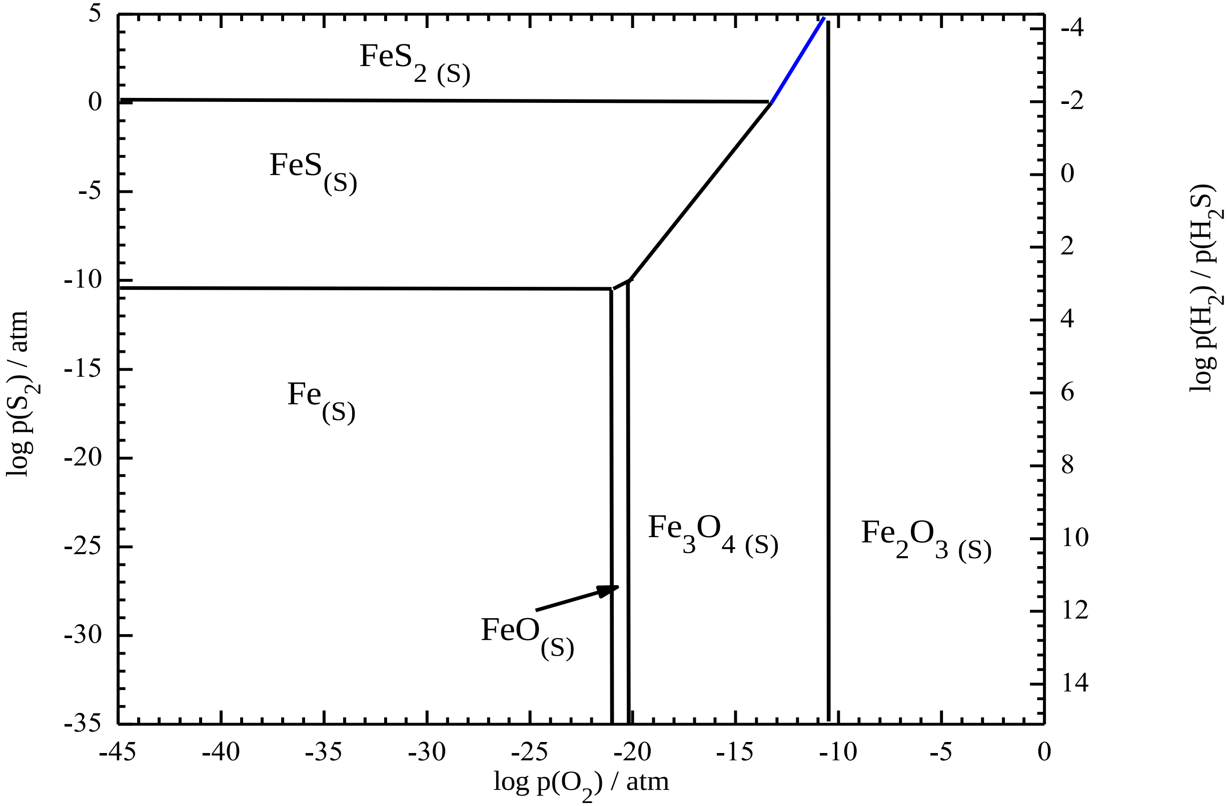
$$Fe_2O_3 + S_2 \Leftrightarrow 2FeS + \tfrac{3}{2}O_2$$

Kellogg diagrams



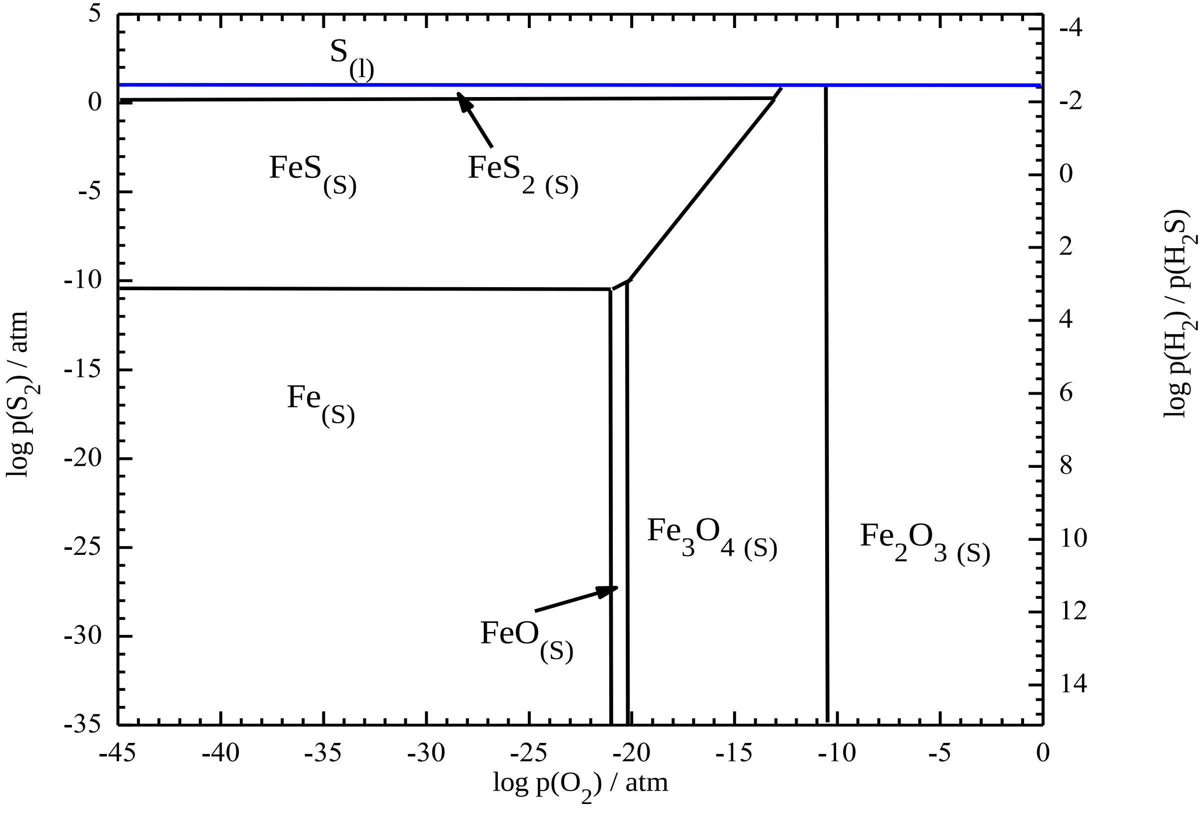
$$FeS + \frac{1}{2}S_2 \Leftrightarrow FeS_2$$

Kellogg diagrams



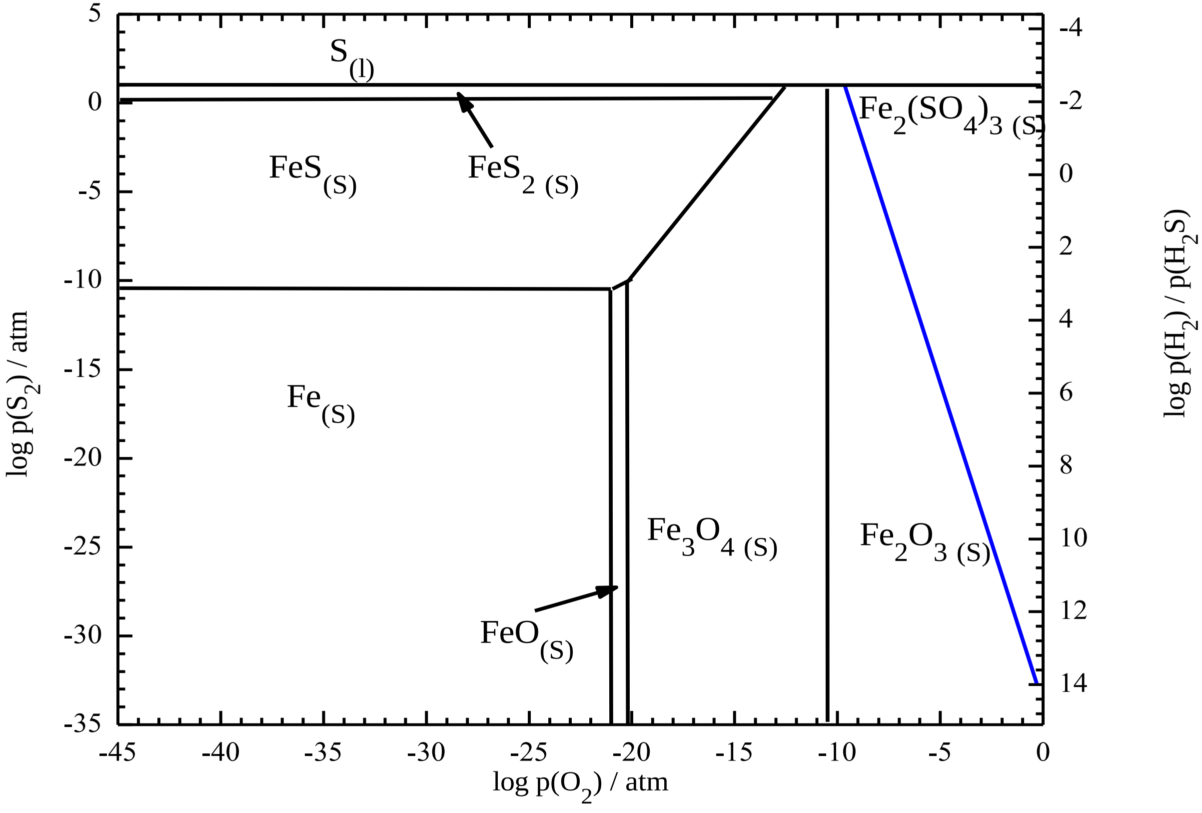
$$Fe_3O_4 + 3S_2 \Leftrightarrow 3FeS_2 + 2O_2$$

Kellogg diagrams



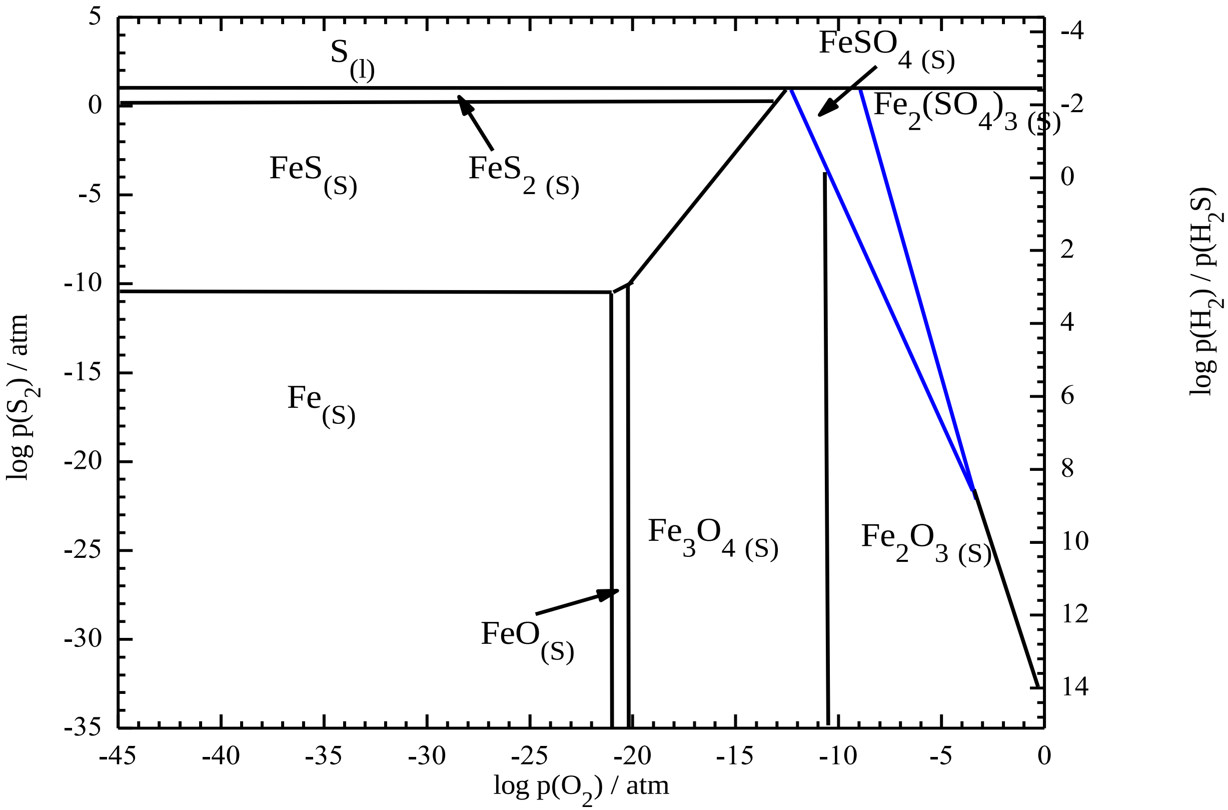
$$\tfrac{1}{2}S_2 \Leftrightarrow S_{liq}$$

Kellogg diagrams



$$Fe_2O_3 + \tfrac{3}{2}S_2 + \tfrac{9}{2}O_2 \Leftrightarrow Fe_2(SO_4)_3$$

Kellogg diagrams

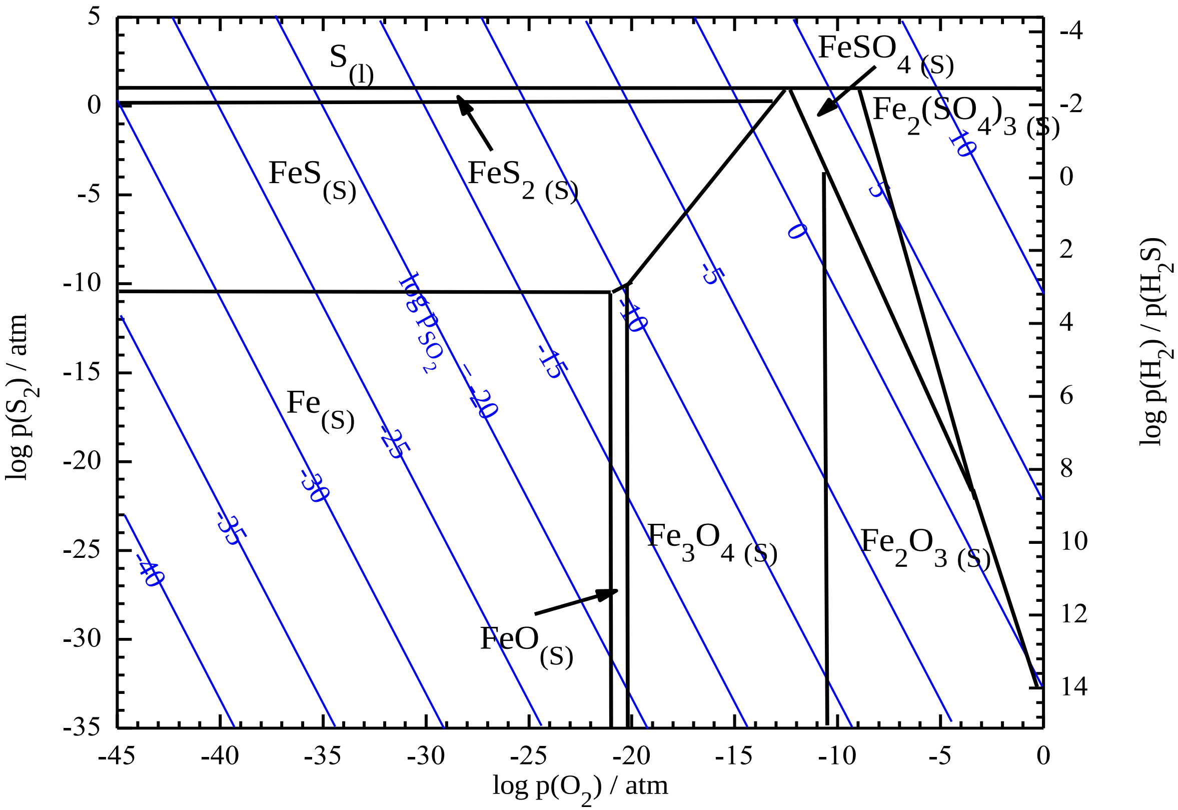


$$2FeSO_4 + \tfrac{1}{2}S_2 + 2O_2 \Leftrightarrow Fe_2(SO_4)_3$$

$$Fe_2O_3 + S_2 + \tfrac{5}{2}O_2 \Leftrightarrow 2FeSO_4$$

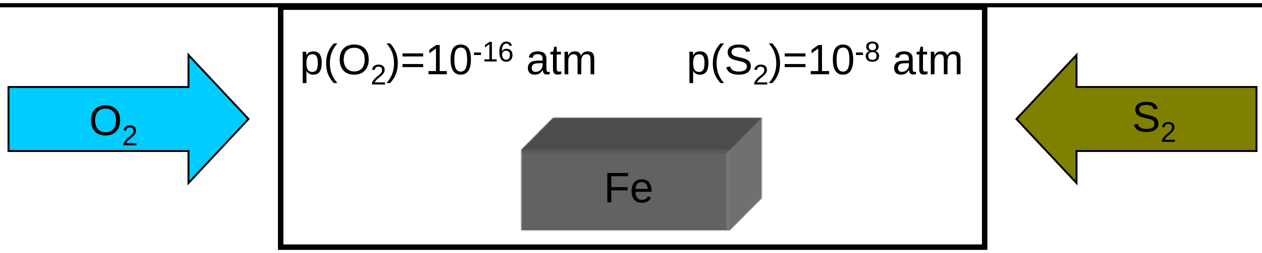
$$Fe_3O_4 + \tfrac{3}{2}S_2 + 4O_2 \Leftrightarrow 3FeSO_4$$

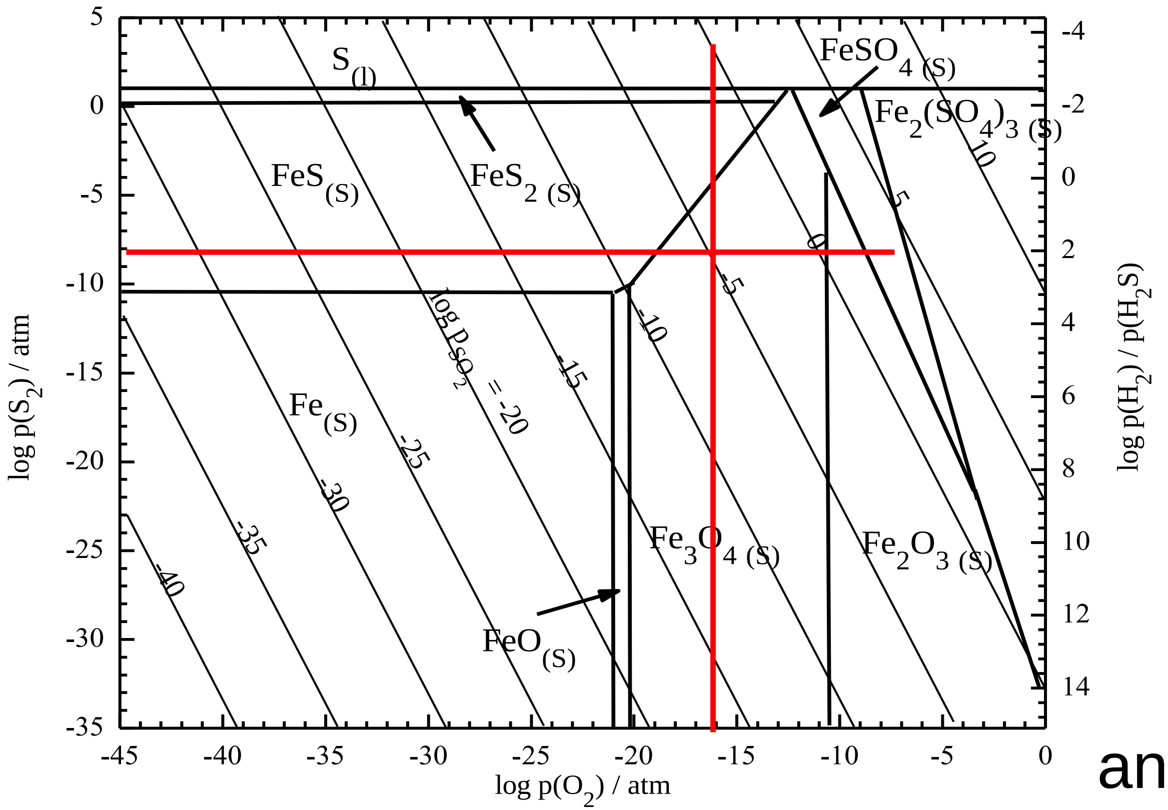
Kellogg diagrams



$$O_2 + \tfrac{1}{2}S_2 \Leftrightarrow SO_2$$

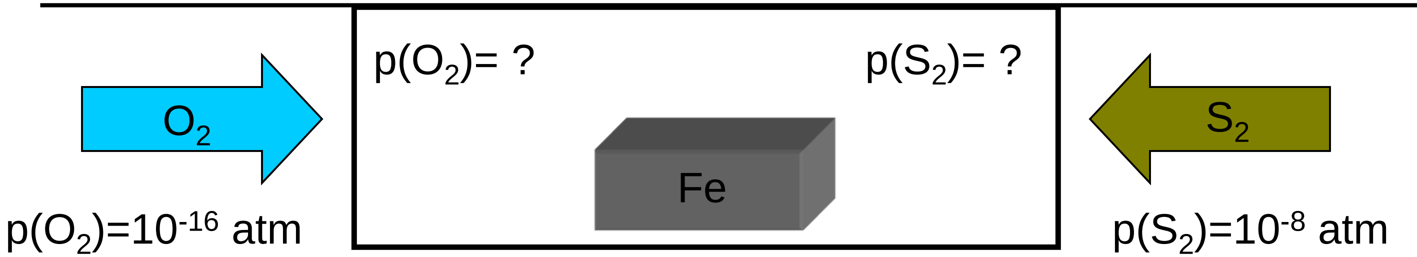
Kellogg diagrams

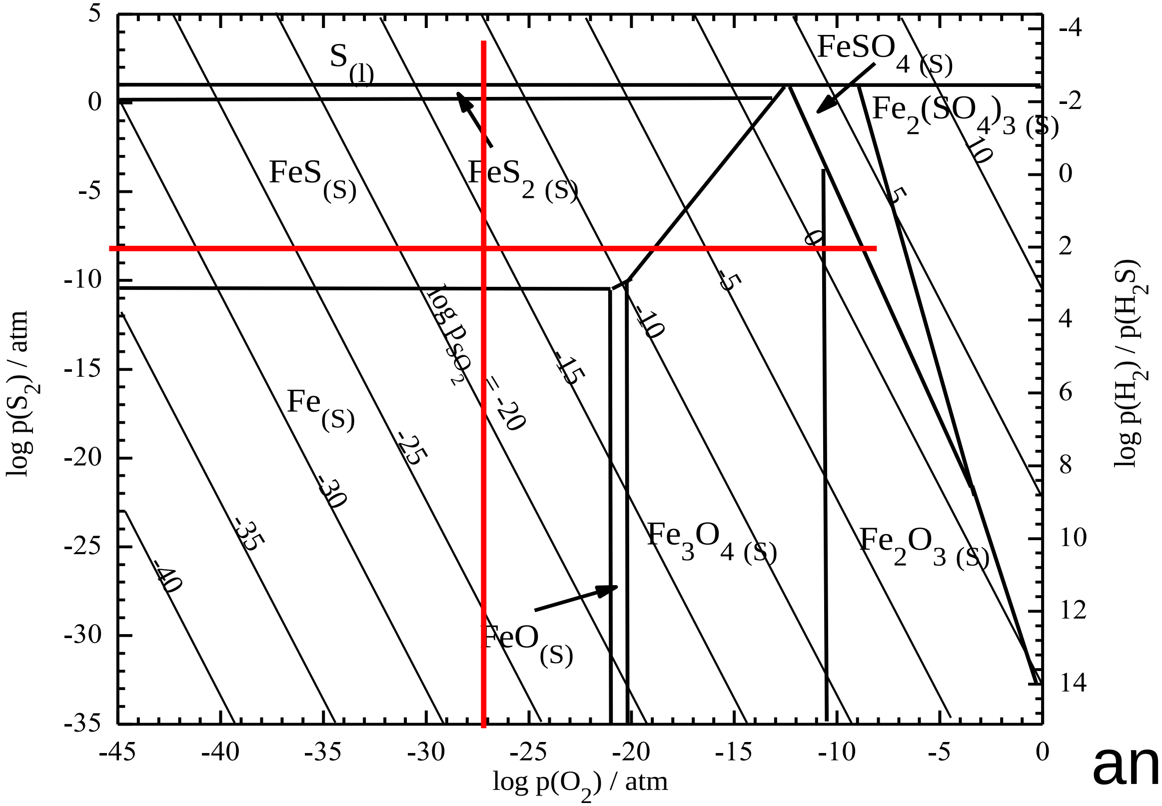




answer.: Fe ⟶ Fe_3O_4

Kellogg diagrams





answer: Fe ⟶ FeS

Gas partial pressure in mixtures

Oxygen-sulfur system

(1) $S_2 + \frac{1}{2}O_2 \Leftrightarrow S_2O$

$$p_{O_2} = \left(\frac{p_{S_2O}}{p_{S_2}}\right)^2 \cdot \exp\left(\frac{2\Delta G_1^0}{RT}\right)$$

(2) $S_2O + \frac{1}{2}O_2 \Leftrightarrow 2SO$

$$p_{O_2} = \left(\frac{p_{SO}^2}{p_{S_2O}}\right)^2 \cdot \exp\left(\frac{2\Delta G_2^0}{RT}\right)$$

(3) $SO + \frac{1}{2}O_2 \Leftrightarrow SO_2$

$$p_{O_2} = \left(\frac{p_{SO_2}}{p_{SO}}\right)^2 \cdot \exp\left(\frac{2\Delta G_3^0}{RT}\right)$$

(4) $SO_2 + \frac{1}{2}O_2 \Leftrightarrow SO_3$

$$p_{O_2} = \left(\frac{p_{SO_3}}{p_{SO_2}}\right)^2 \cdot \exp\left(\frac{2\Delta G_4^0}{RT}\right)$$

$$N_S = 2n_{S_2} + 2n_{S_2O} + n_{SO} + n_{SO_2} + n_{SO_3}$$

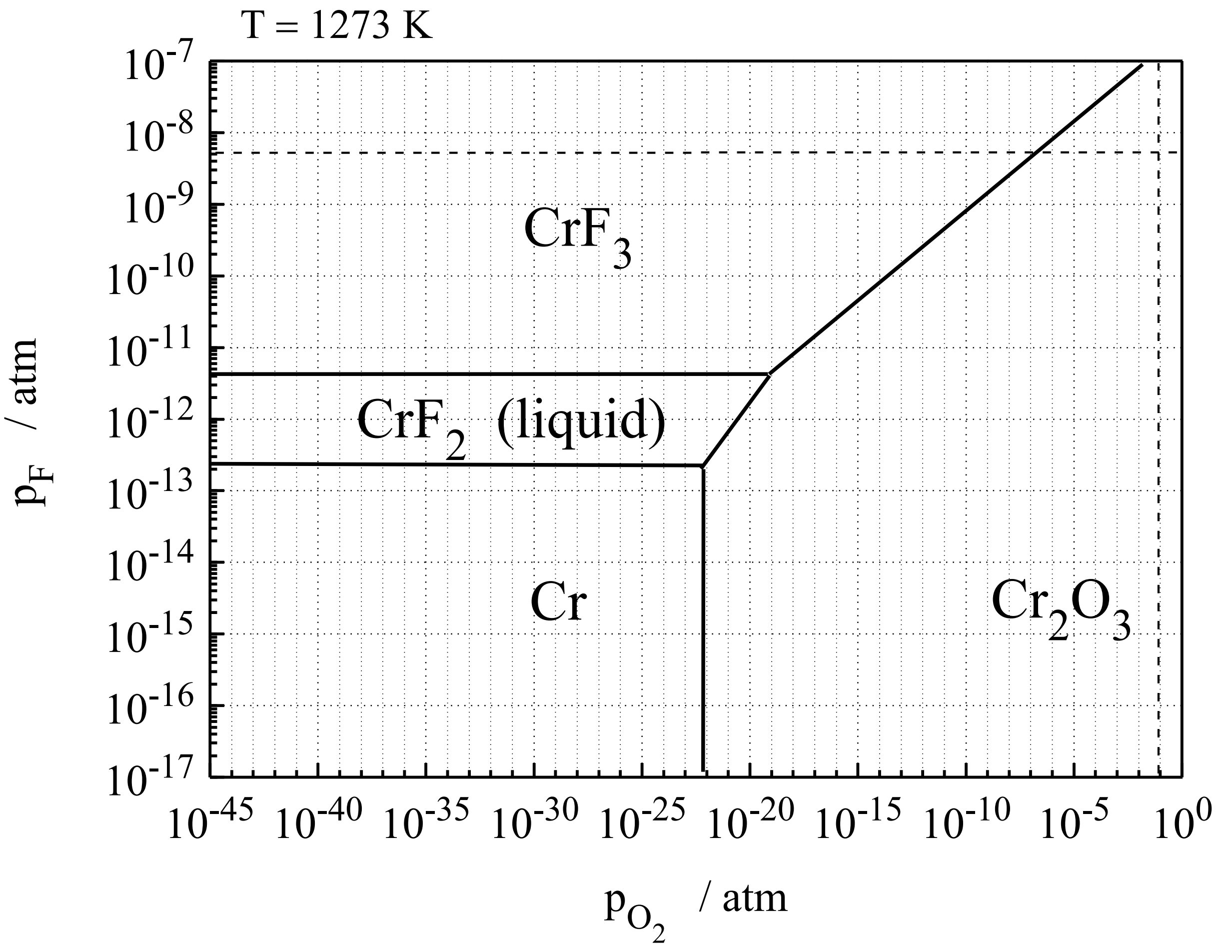
$$N_{O_2} = n_{O_2} + \frac{1}{2}n_{S_2O} + \frac{1}{2}n_{SO} + n_{SO_2} + \frac{3}{2}n_{SO_3}$$

N_s and N_{O_2} denote total number of S i O_2 moles present in the system,
n_{S_2}, n_{S_2O}, n_{SO}, n_{SO_2}, n_{SO_3}, n_{O_2} – number of moles for individual gases at thermodynamic equilibrium.

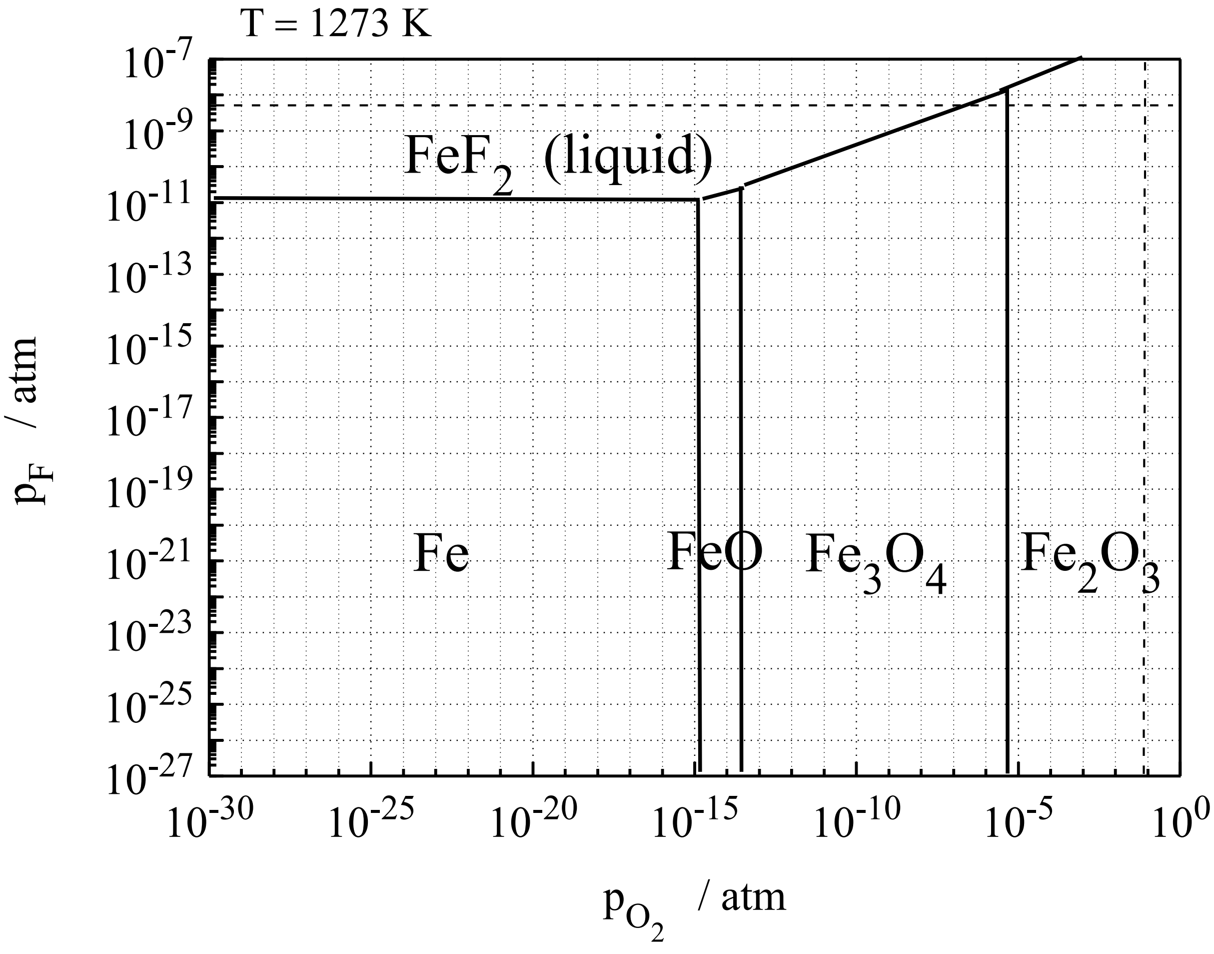
$$p_i = \frac{n_i}{\sum_{i=1}^{m} n_i} \cdot p_{tot}$$

where: n_i is the number of moles for the i component,
m – number of all components in the system,
p_{tot} denotes the total pressure of the gas mixture.

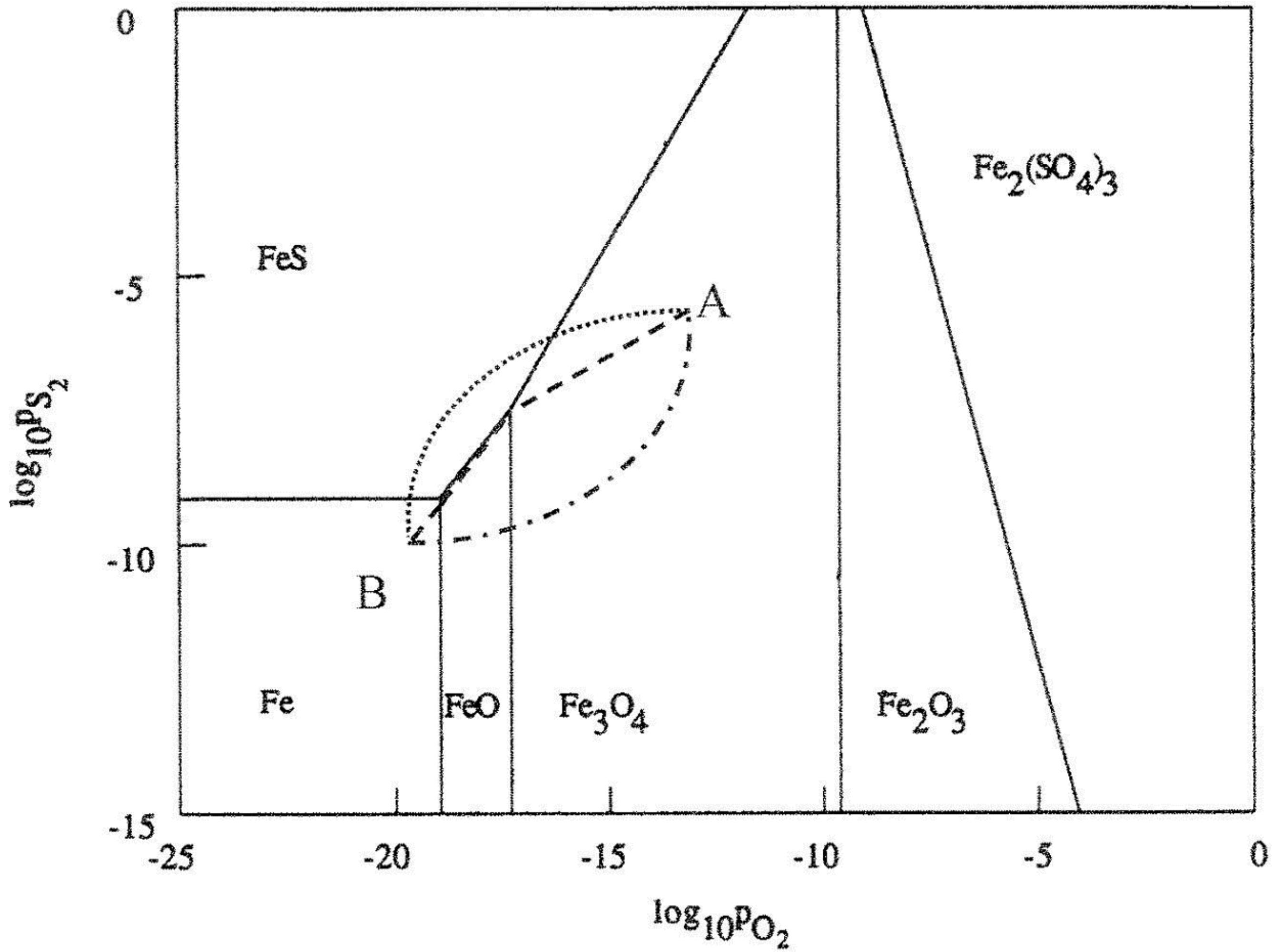
Kellogg diagrams



Kellogg diagrams

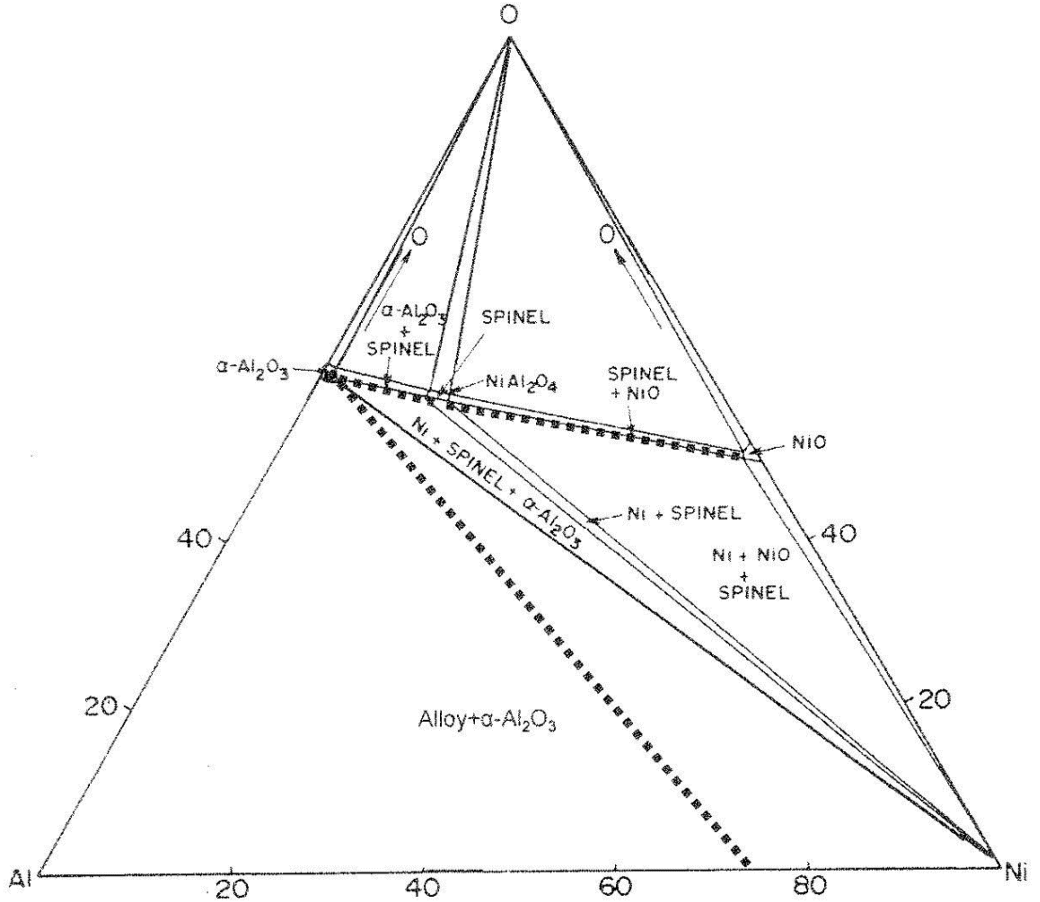


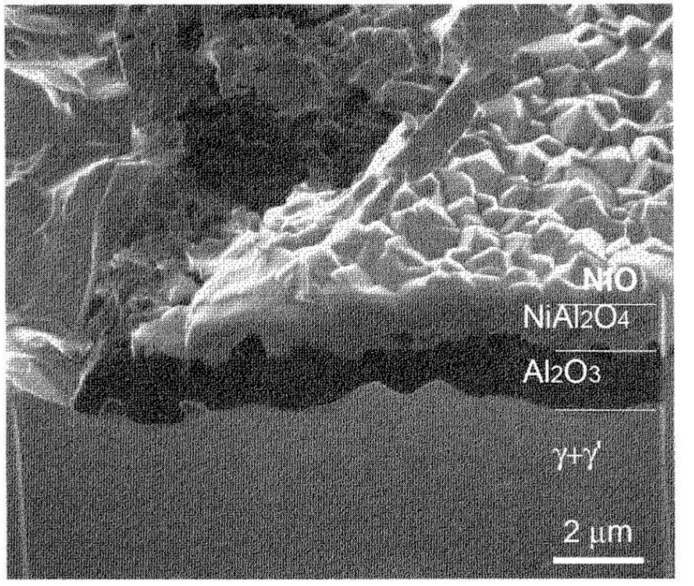
Kellogg diagram for the Fe-O-S system at 800 °C, which illustrates three possible diffusion paths for the reaction with the A component gas



David J. Young, „High temperature oxidation and corrosion of metals”, Elsevier, Sydney 2016.

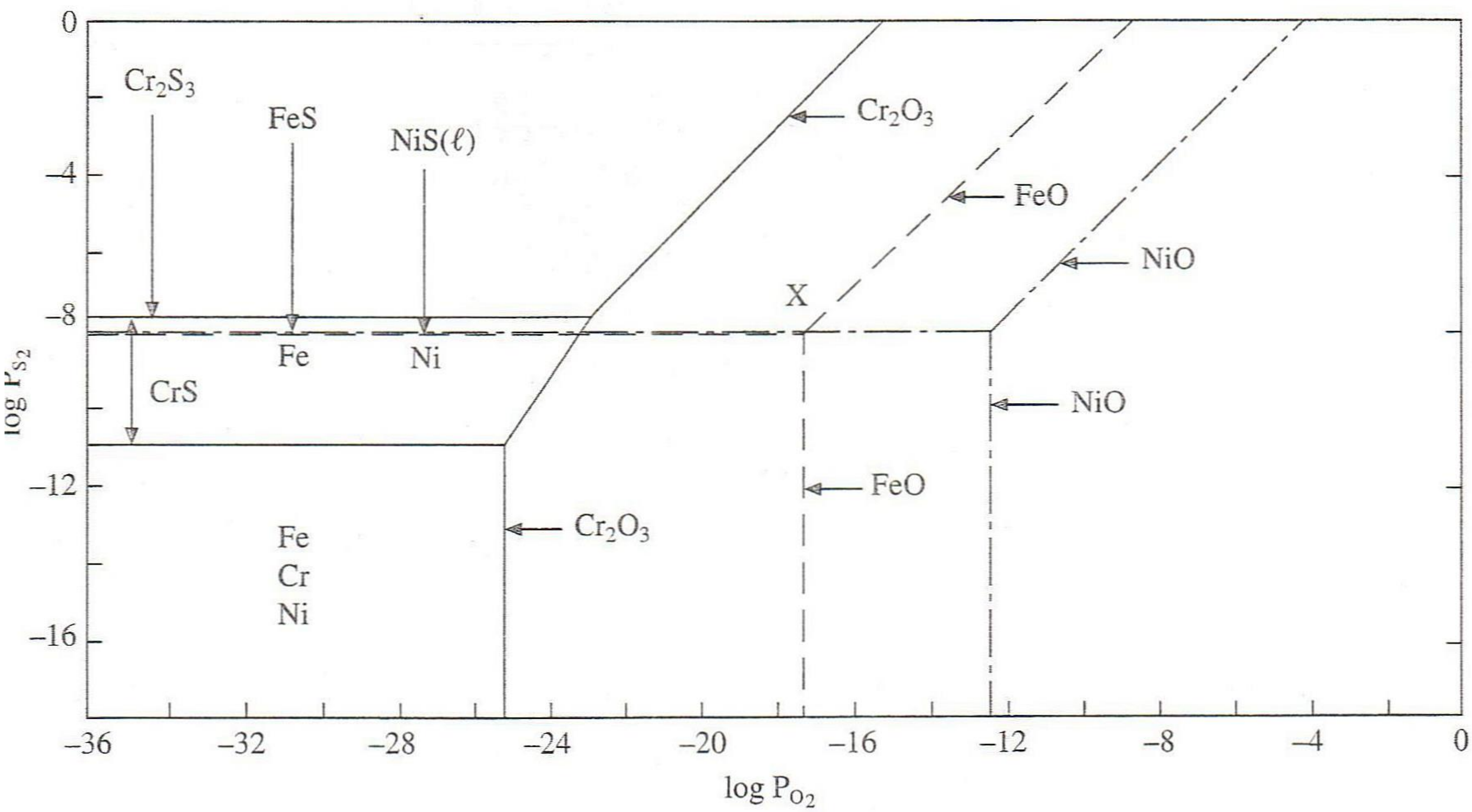
Phase diagram of the Al-Ni-O system at 1000 ºC and the cross-section of the oxide scale formed on Ni-22Al





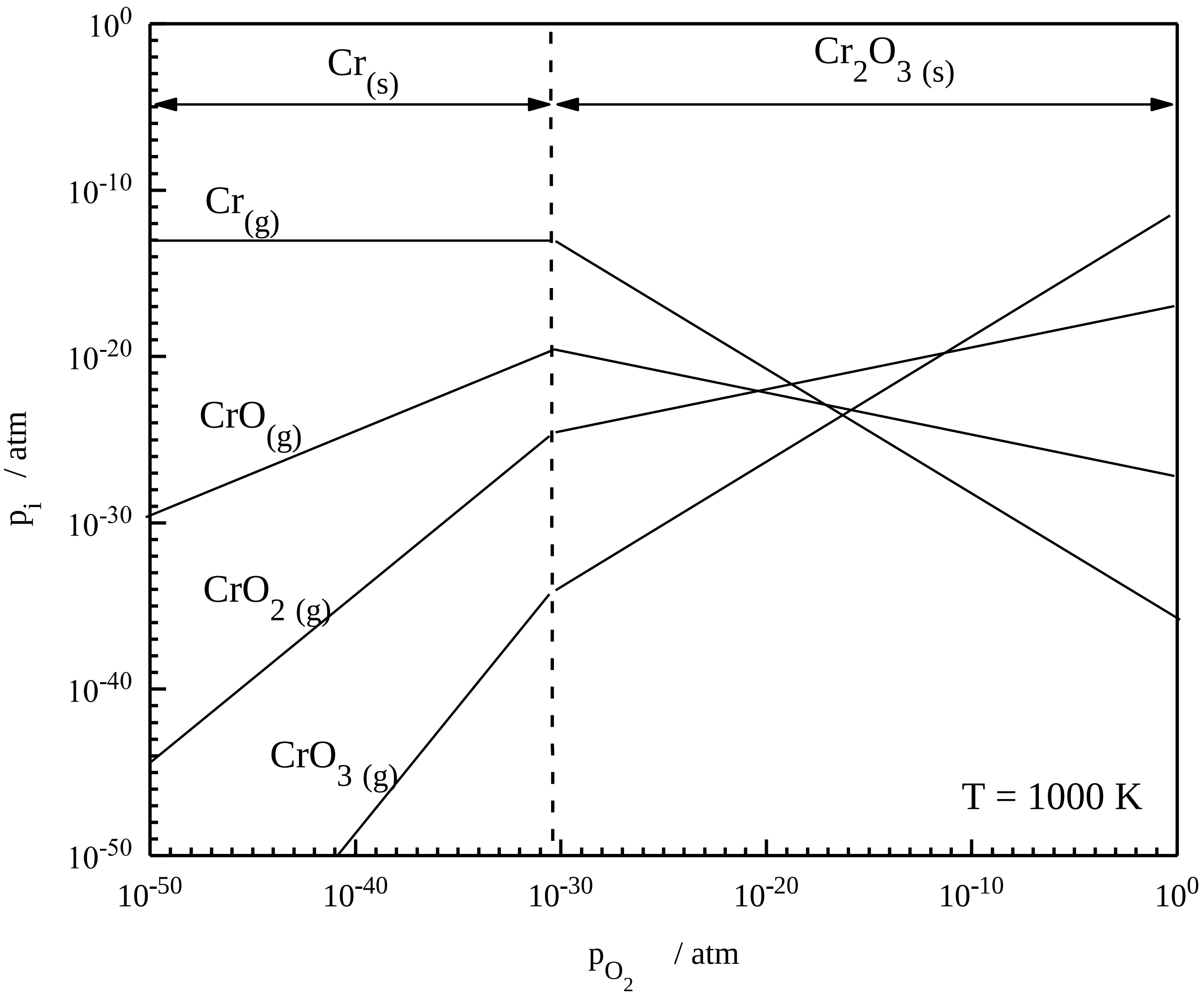
David J. Young, „High temperature oxidation and corrosion of metals", Elsevier, Sydney 2016.

Kellogg diagram of the (Fe-Cr-Ni)-O-S system at 870 ^{o}C



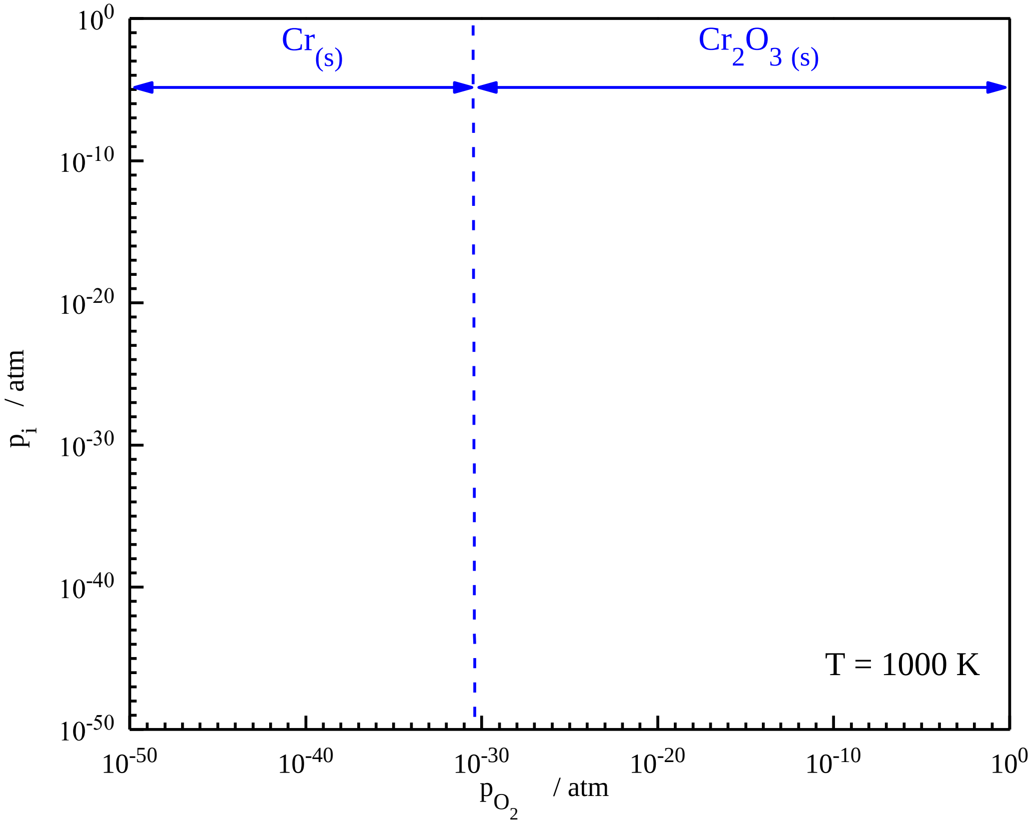
A.S. Khanna, Introduction to High Temperature Oxidation and Corrosion, ASM International, Materials Park, 2002.

Pressures of volatile oxides



Z. Grzesik, "Thermodynamics of gaseous corrosion" in ASM Handbook, vol. 13a, p.90-96, ASM International, Materials Park, Ohio, USA, 2003.

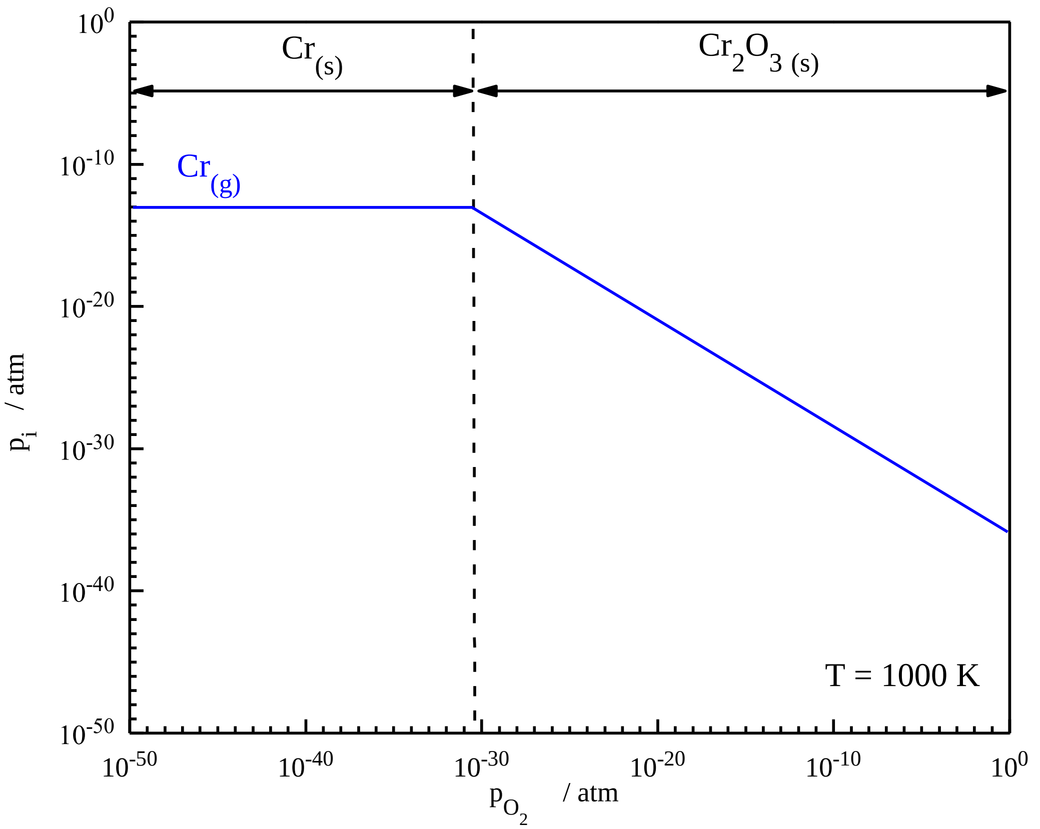
Pressures of volatile oxides



$$2Cr_{(s)} + \tfrac{3}{2}O_2 \Leftrightarrow Cr_2O_{3(s)}$$

$$p_{O_2} = \exp\left(\frac{2\Delta G^0}{3RT}\right)$$

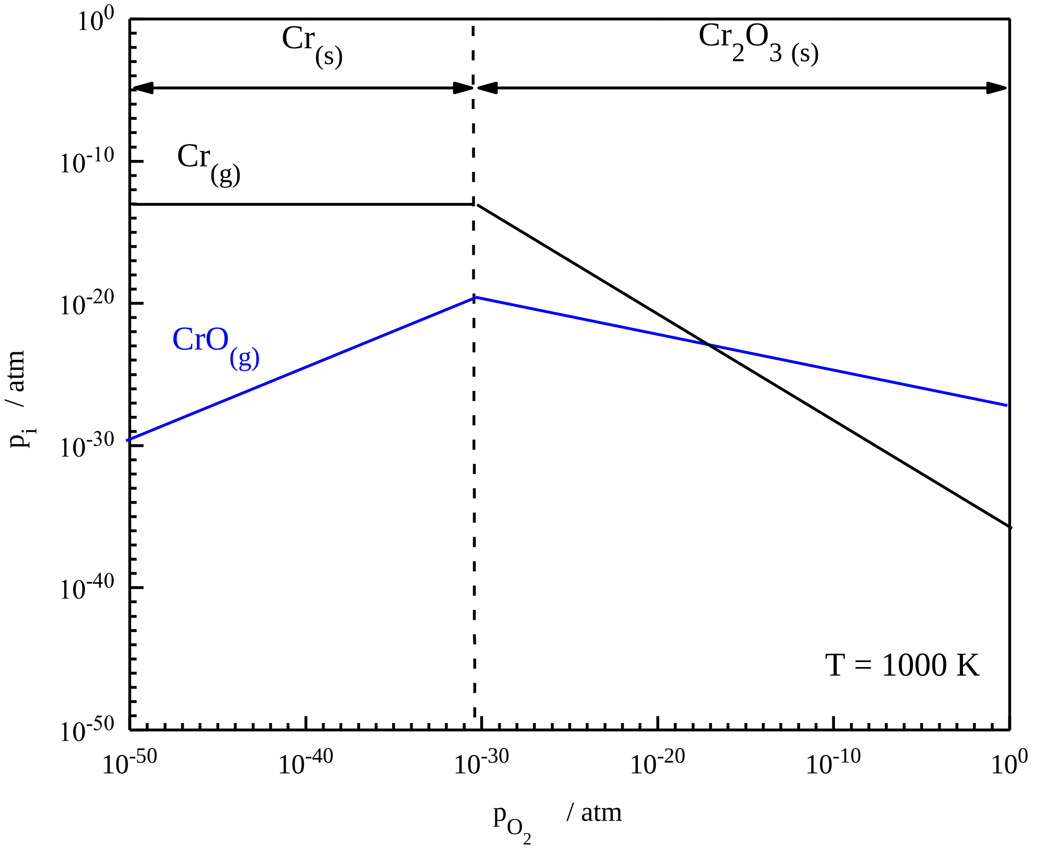
Pressures of volatile oxides



$$Cr_{(s)} \Leftrightarrow Cr_{(g)} \qquad Cr_2O_{3(s)} \Leftrightarrow 2Cr_{(g)} + \tfrac{3}{2}O_2$$

$$p_{Cr_{(g)}} = \exp\left(-\frac{\Delta G^0}{RT}\right) \qquad p_{Cr_{(g)}} = p_{O_2}^{-\frac{3}{4}} \exp\left(-\frac{\Delta G^0}{2RT}\right)$$

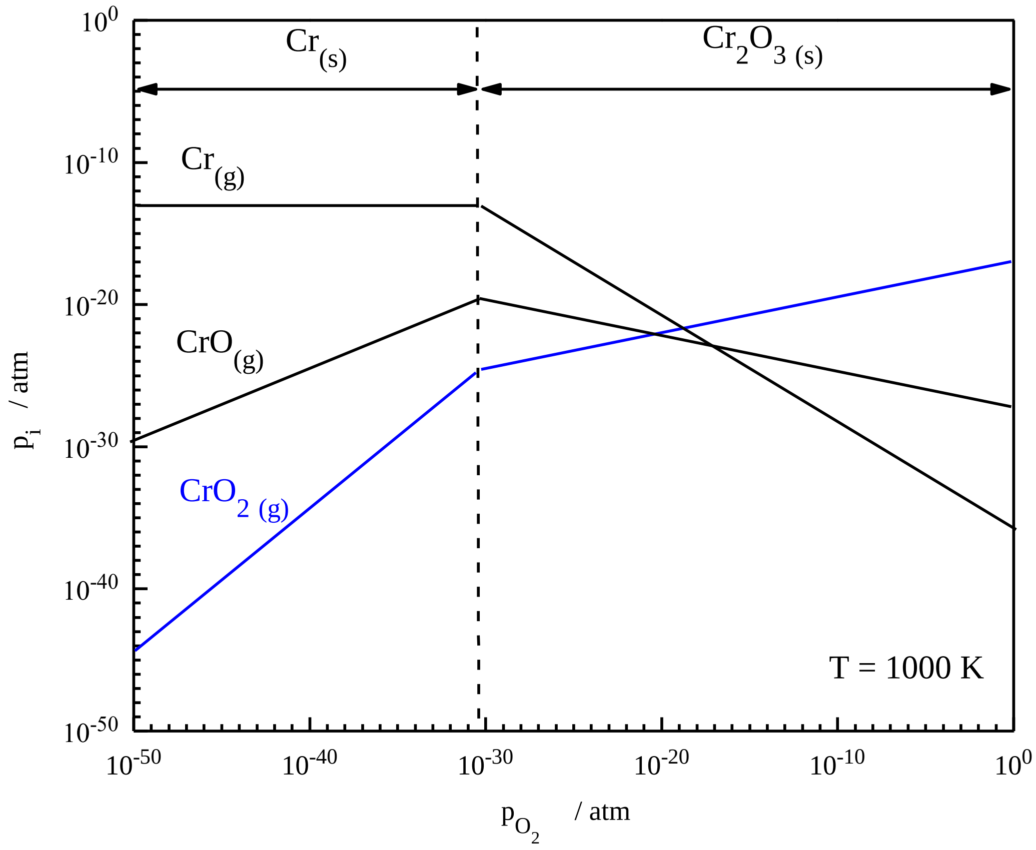
Pressures of volatile oxides



$$Cr_{(s)} + \tfrac{1}{2}O_2 \Leftrightarrow CrO_{(g)} \qquad Cr_2O_{3(s)} \Leftrightarrow 2CrO_{(g)} + \tfrac{1}{2}O_2$$

$$p_{CrO\,(g)} = p_{O_2}^{\frac{1}{2}} \exp\left(-\frac{\Delta G^0}{RT}\right) \qquad p_{CrO\,(g)} = p_{O_2}^{-\frac{1}{4}} \exp\left(-\frac{\Delta G^0}{2RT}\right)$$

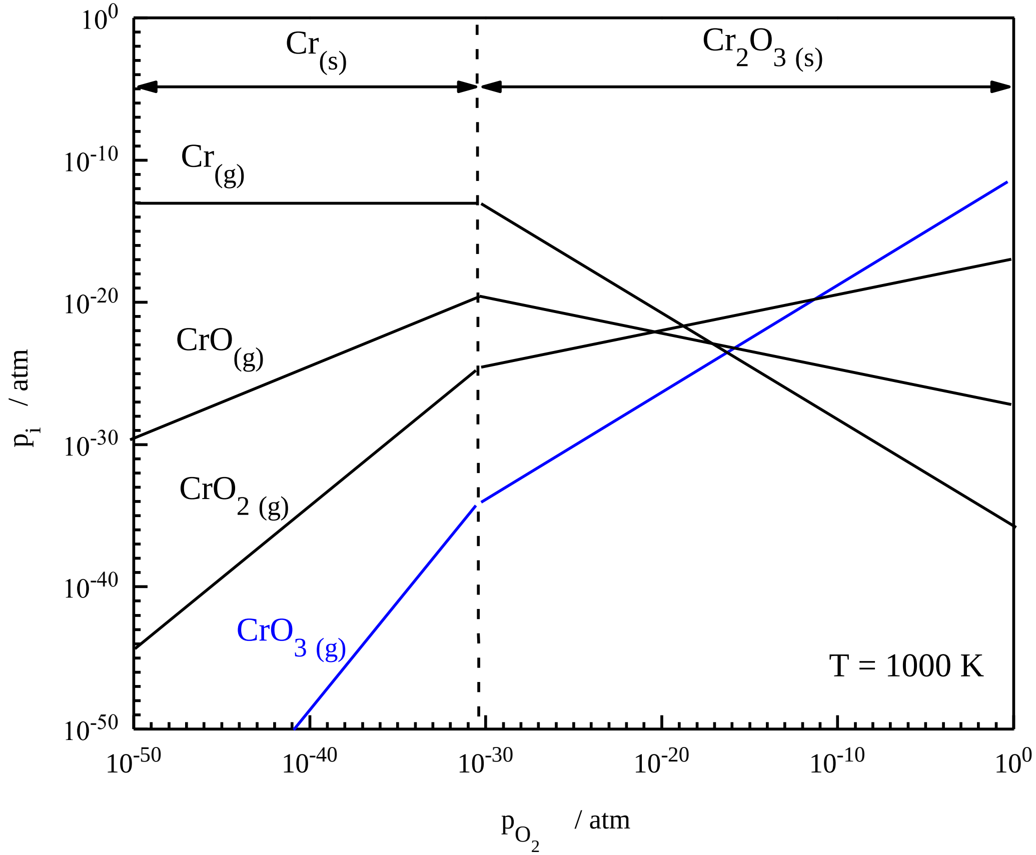
Pressures of volatile oxides



$$Cr_{(s)} + O_2 \Leftrightarrow CrO_{2\,(g)} \qquad Cr_2O_{3\,(s)} \Leftrightarrow 2CrO_{2\,(g)} - \tfrac{1}{2}O_2$$

$$p_{CrO_{2\,(g)}} = p_{O_2}\exp\left(-\frac{\Delta G^0}{RT}\right) \qquad p_{CrO_{2\,(g)}} = p_{O_2}^{\frac{1}{4}}\exp\left(-\frac{\Delta G^0}{2RT}\right)$$

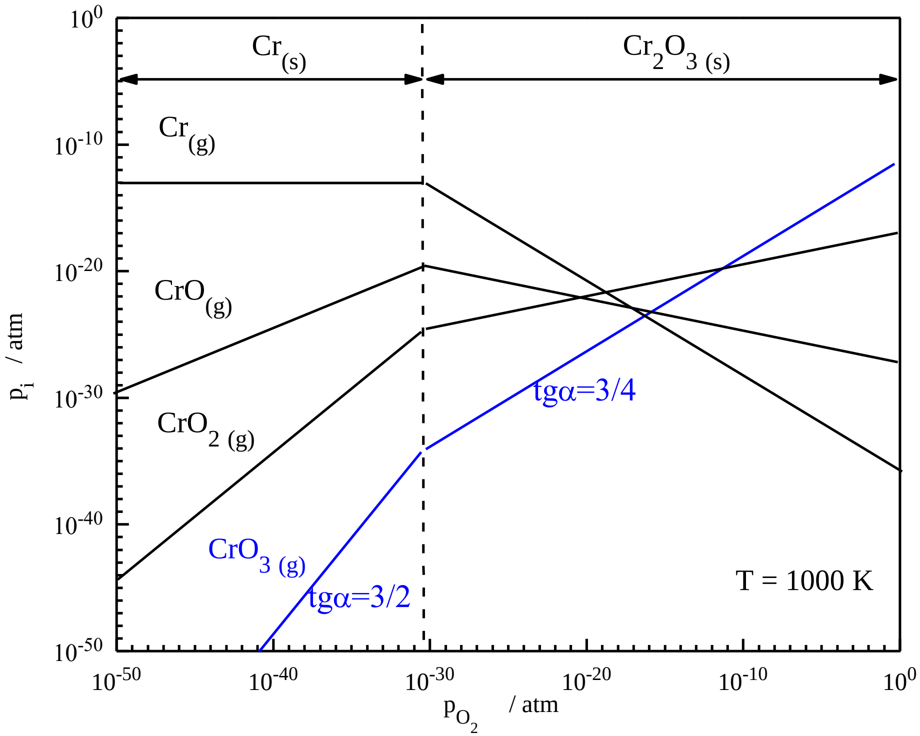
Pressures of volatile oxides



$$Cr_{(s)} + \frac{3}{2}O_2 \Leftrightarrow CrO_{3(g)} \qquad Cr_2O_{3(s)} \Leftrightarrow 2CrO_{3(g)} - \frac{3}{2}O_2$$

$$p_{CrO_{3(g)}} = p_{O_2}^{\frac{3}{2}} \exp\left(-\frac{\Delta G^0}{RT}\right) \qquad p_{CrO_{3(g)}} = p_{O_2}^{\frac{3}{4}} \exp\left(-\frac{\Delta G^0}{2RT}\right)$$

Pressures of volatile oxides



$$Cr_{(s)} + \tfrac{3}{2} O_2 \Leftrightarrow CrO_{3(g)}$$

$$Cr_2O_{3(s)} \Leftrightarrow 2CrO_{3(g)} - \tfrac{3}{2} O_2$$

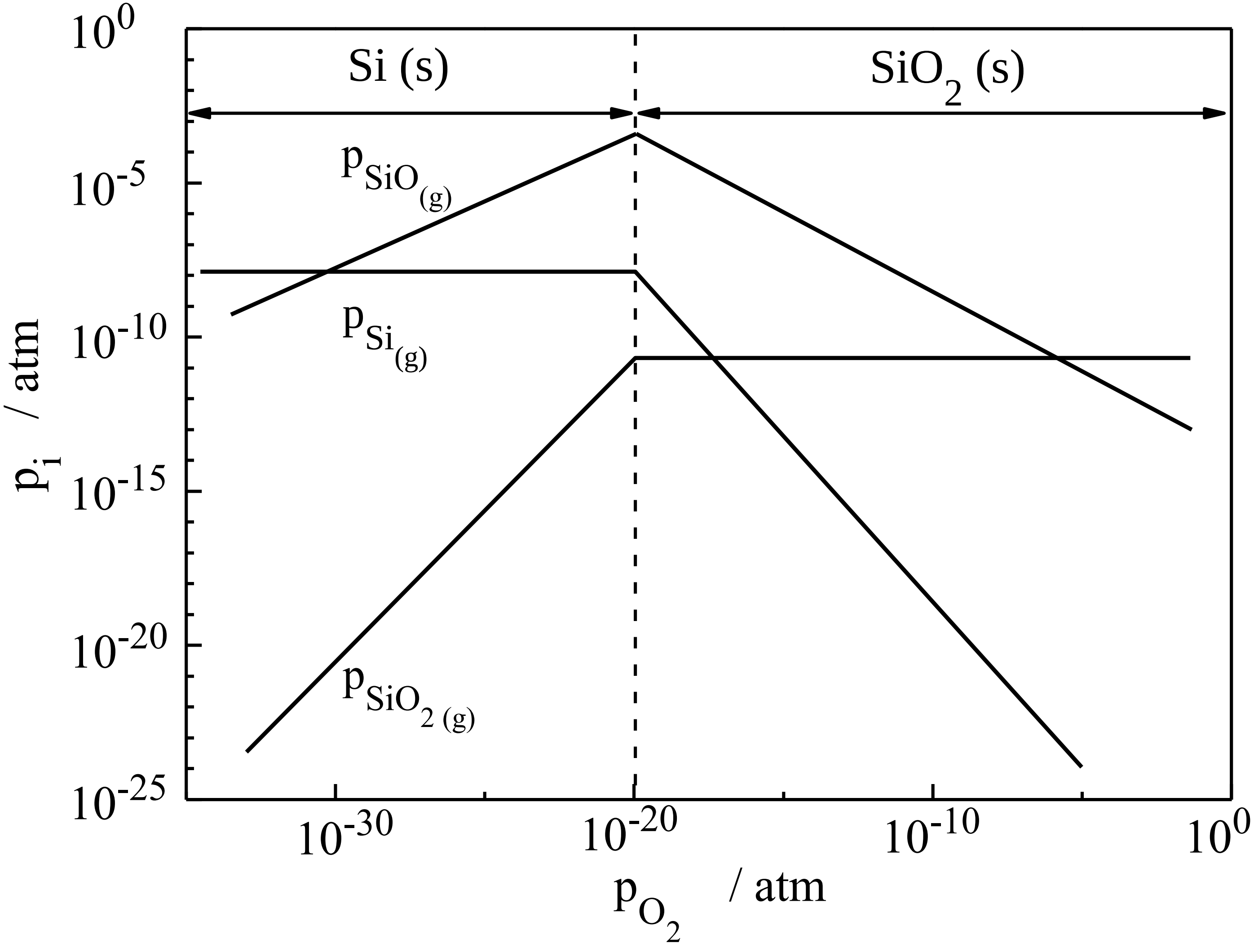
$$p_{CrO_{3(g)}} = p_{O_2}^{\frac{3}{2}} \exp\left(-\frac{\Delta G^0}{RT}\right) = p_{O_2}^{\frac{3}{2}} \cdot const$$

$$p_{CrO_{3(g)}} = p_{O_2}^{\frac{3}{4}} \exp\left(-\frac{\Delta G^0}{2RT}\right) = p_{O_2}^{\frac{3}{4}} \cdot const$$

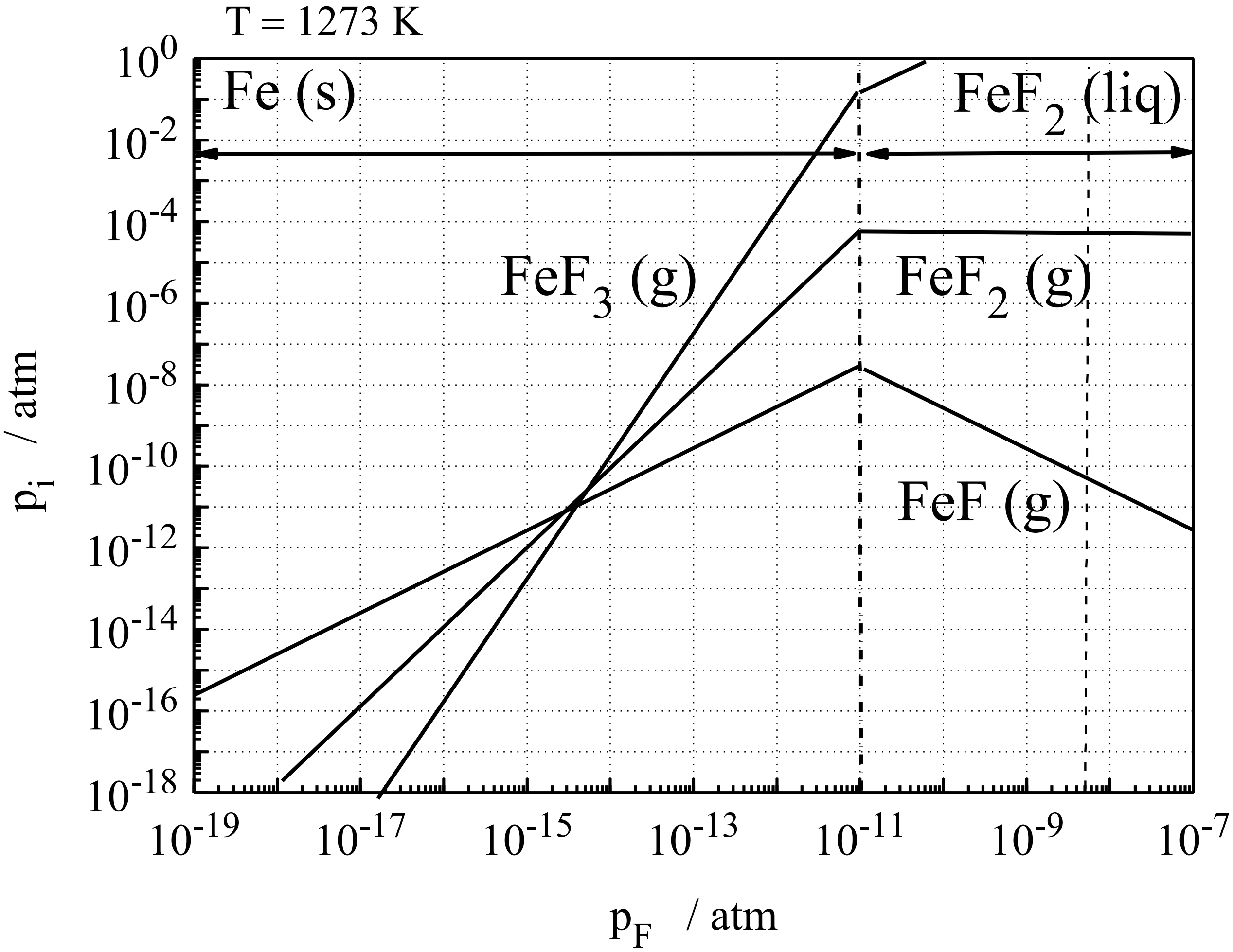
$$\log p_{CrO_{3(g)}} = \tfrac{3}{2} \log p_{O_2} + \log (const)$$

$$\log p_{CrO_{3(g)}} = \tfrac{3}{4} \log p_{O_2} + \log (const)$$

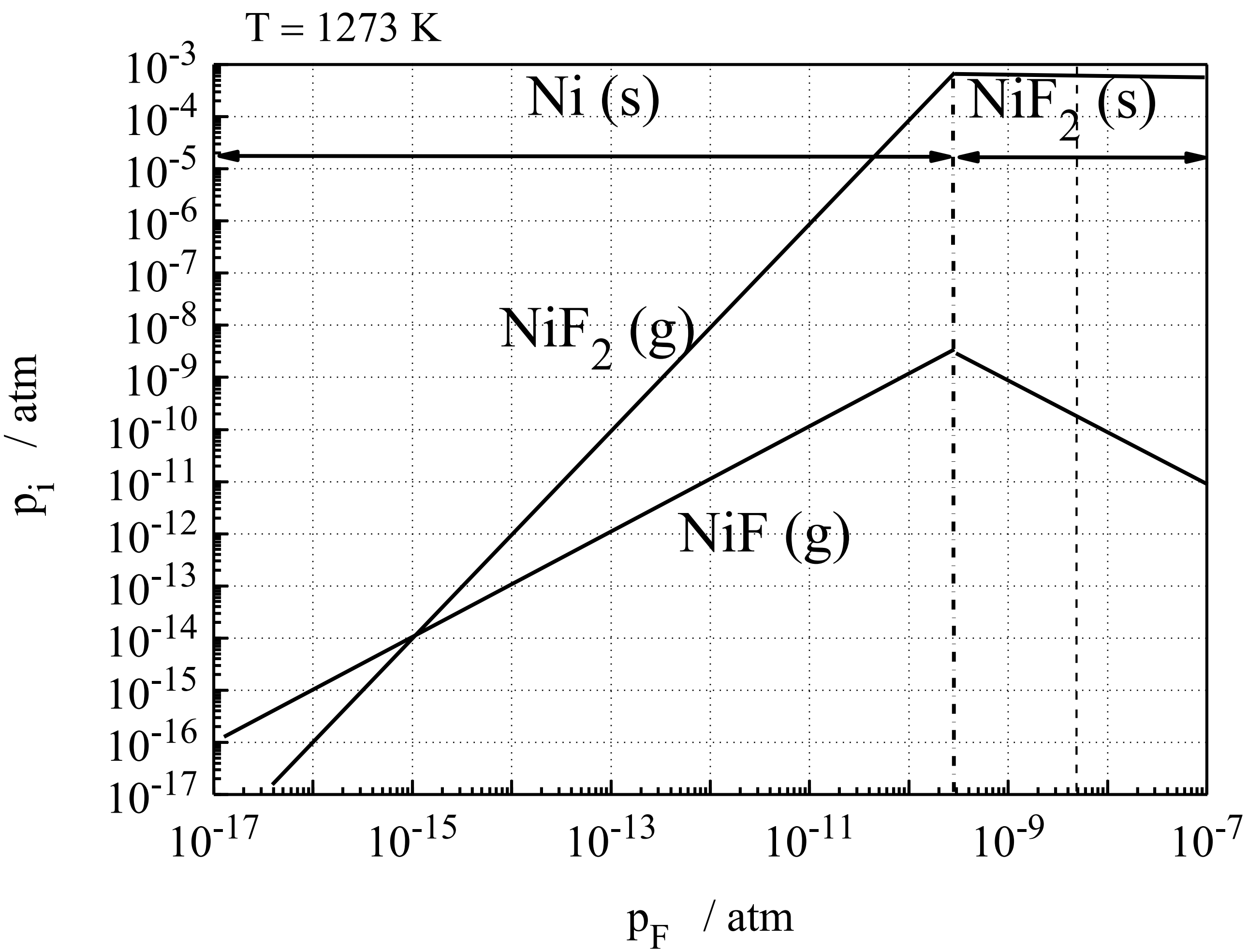
Pressures of volatile oxides



Pressures of volatile oxides



Pressures of volatile oxides



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