

**AGH**

**AKADEMIA GÓRNICZO-HUTNICZA  
IM. STANISŁAWA STASZICA W KRAKOWIE**

**AGH UNIVERSITY OF SCIENCE  
AND TECHNOLOGY**

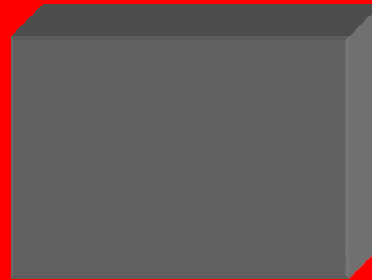
# TERMODYNAMIKA PROCESÓW KORROZJI WYSOKOTEMPERATUROWEJ

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

# Schemat procesu korozji wysokotemperaturowej

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$T = \text{const}$   
 $p = \text{const}$





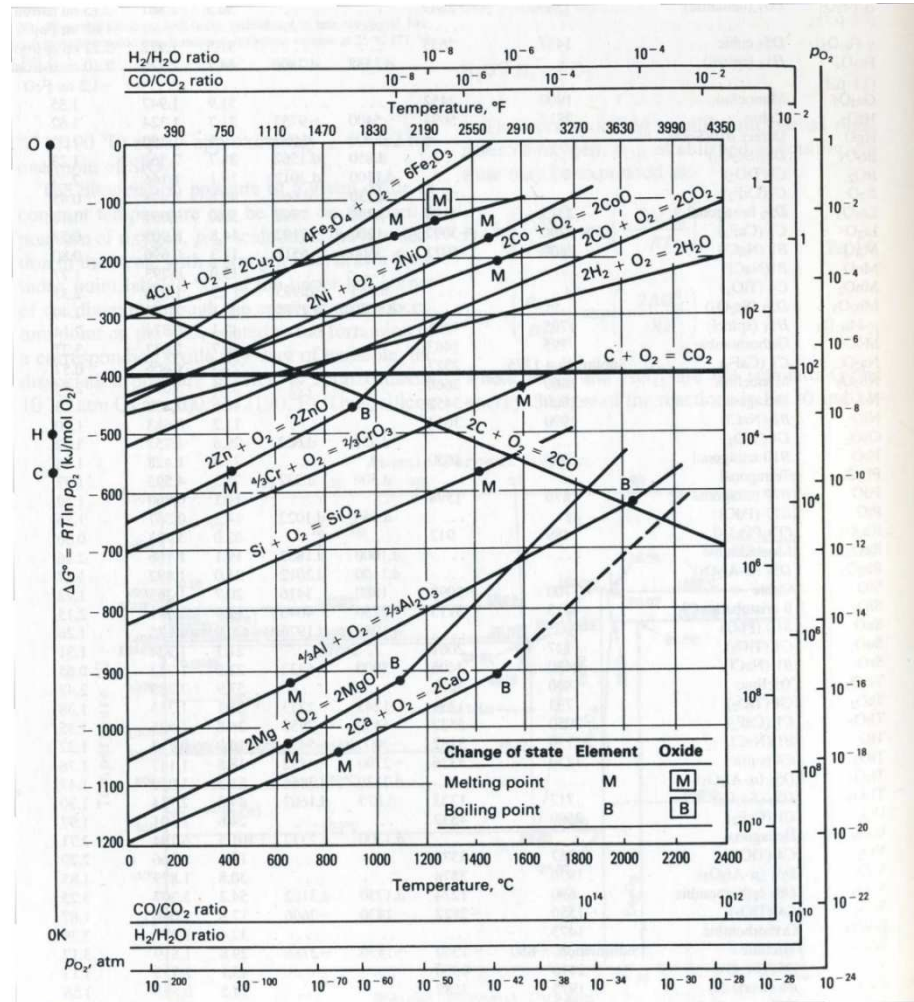
# Diagramy Ellingham'a-Richardson'a (Richardson'a-Jeffes'a)

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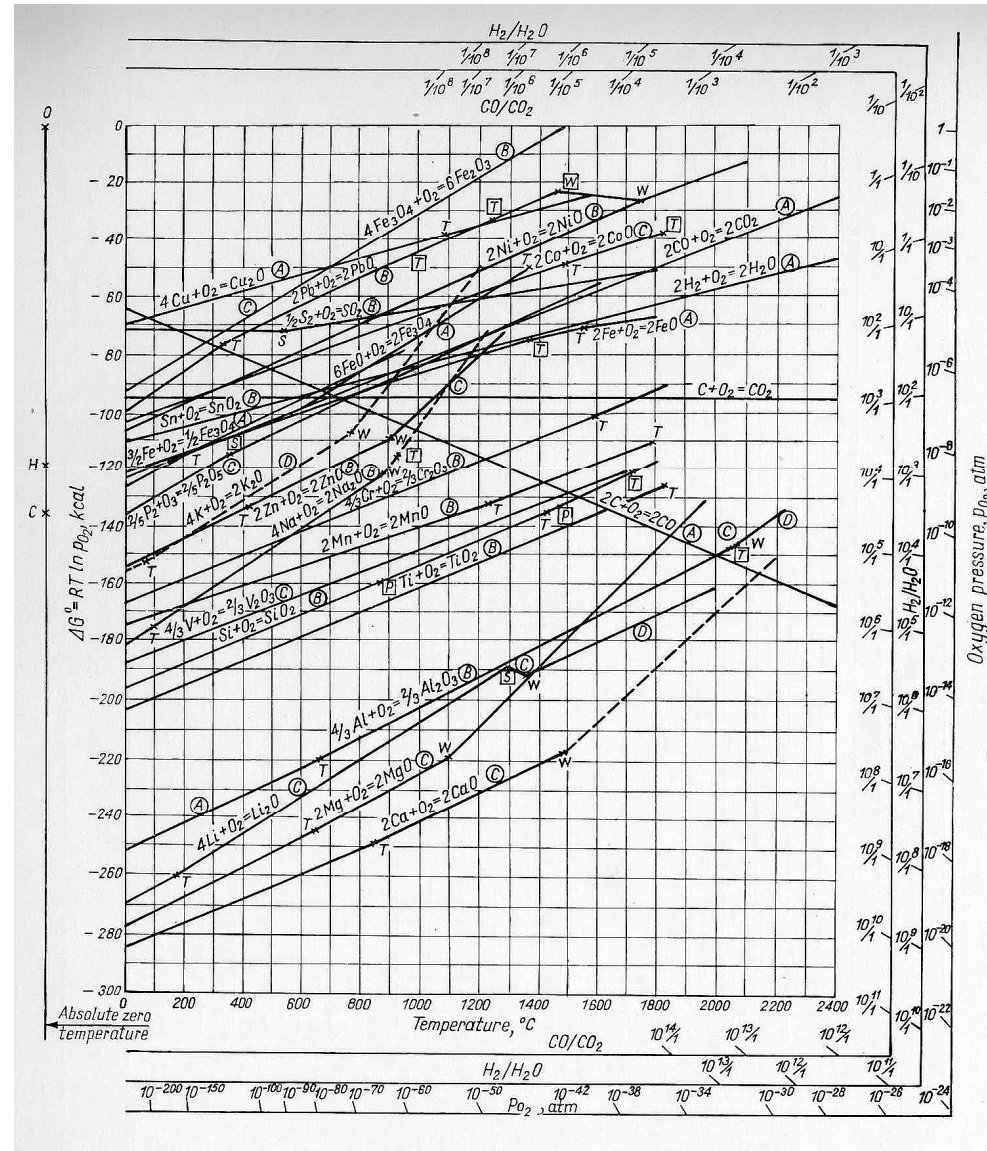
Fizykochemia ciała stałego:  
fizykochemia\_W1\_Stabilność związków nieorganicznych.ppt

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

# Diagramy Ellingham'a-Richardson'a (Richardson'a-Jeffes'a)



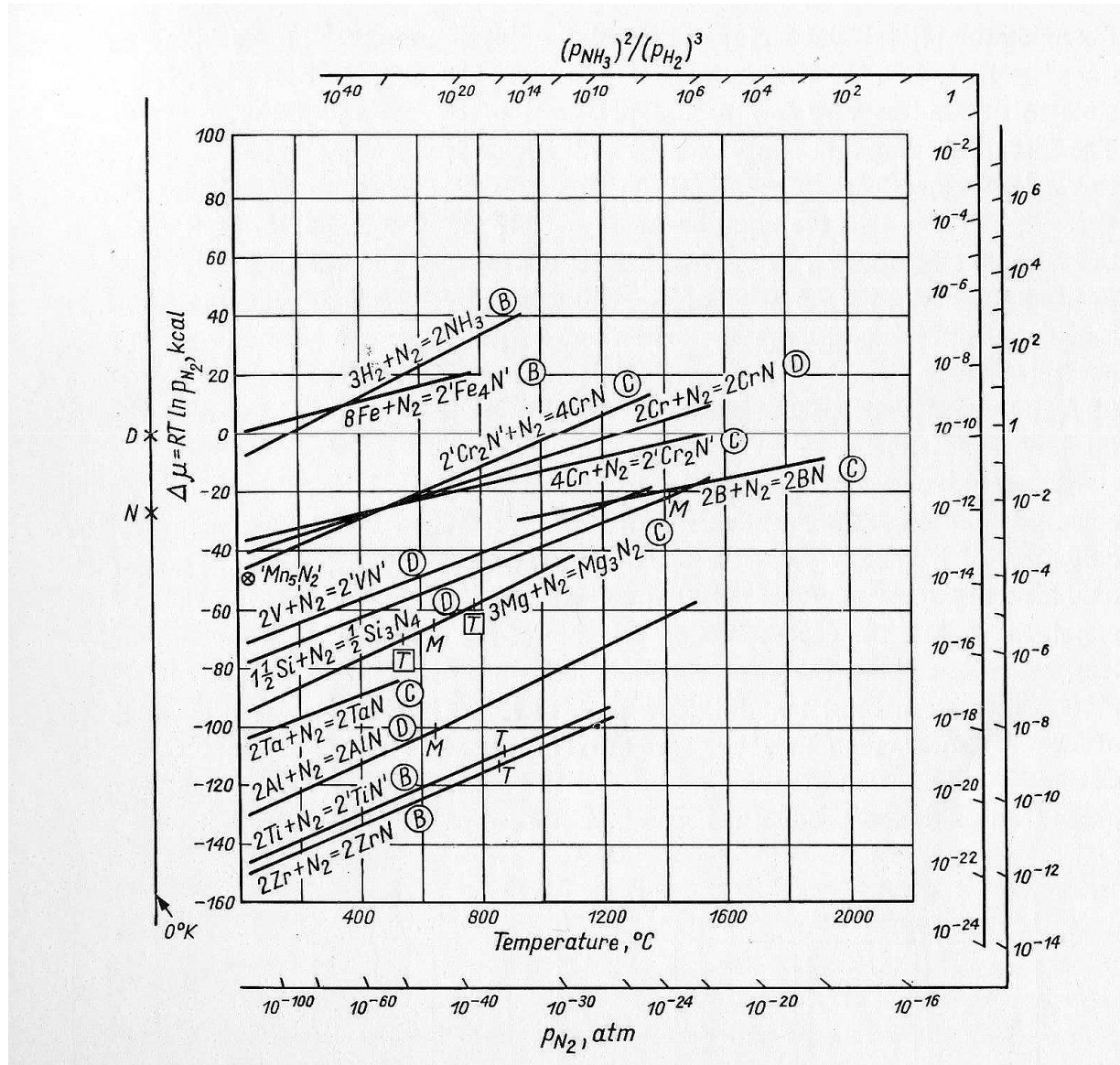
# Diagramy Ellingham'a-Richardson'a (Richardson'a-Jeffes'a)





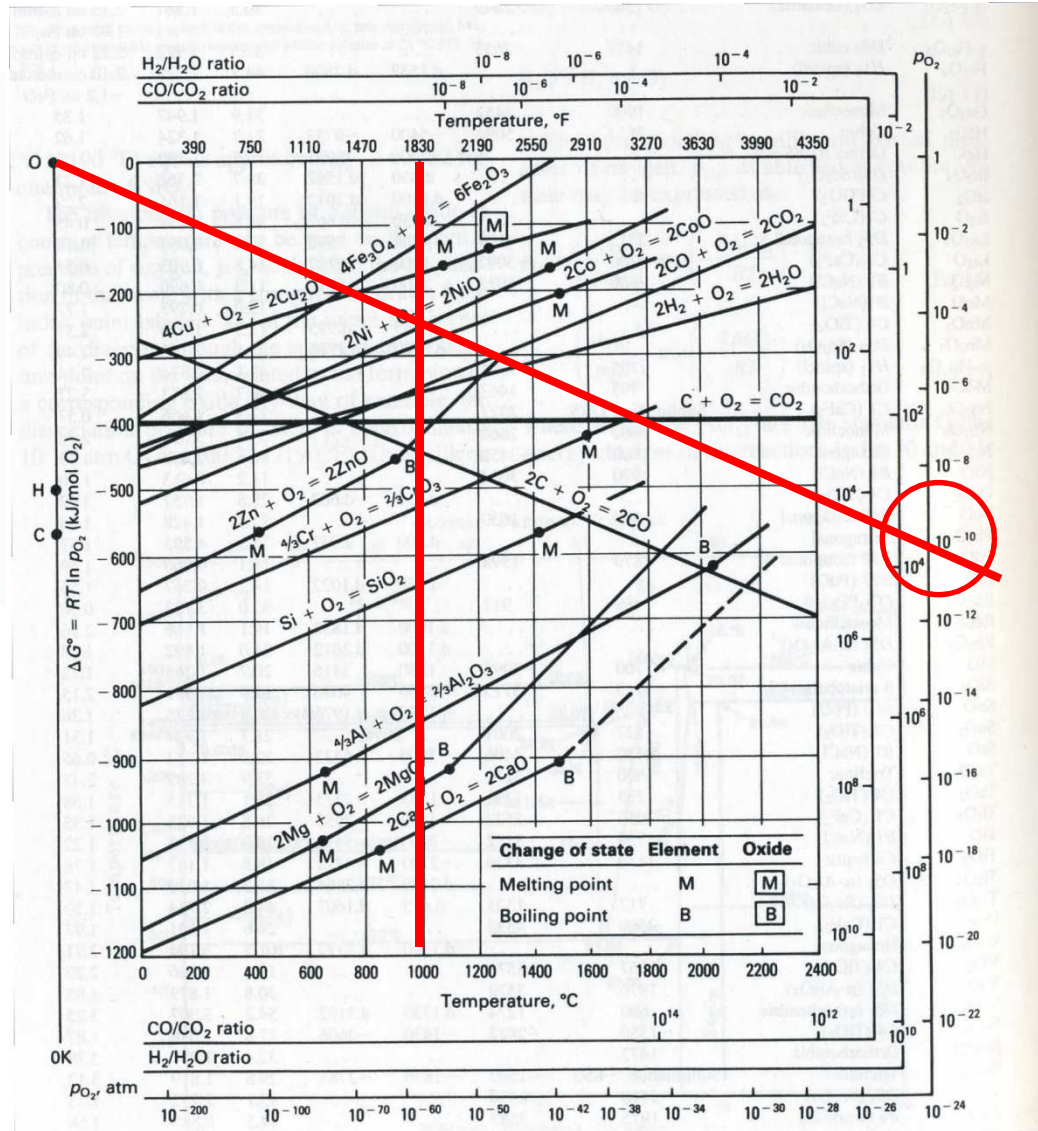


# Diagramy Ellingham'a-Richardson'a (Richardson'a-Jeffes'a)





# Określanie ciśnień dysocjacyjnych



Przykład:

określić ciśnienie dysocjacyjne

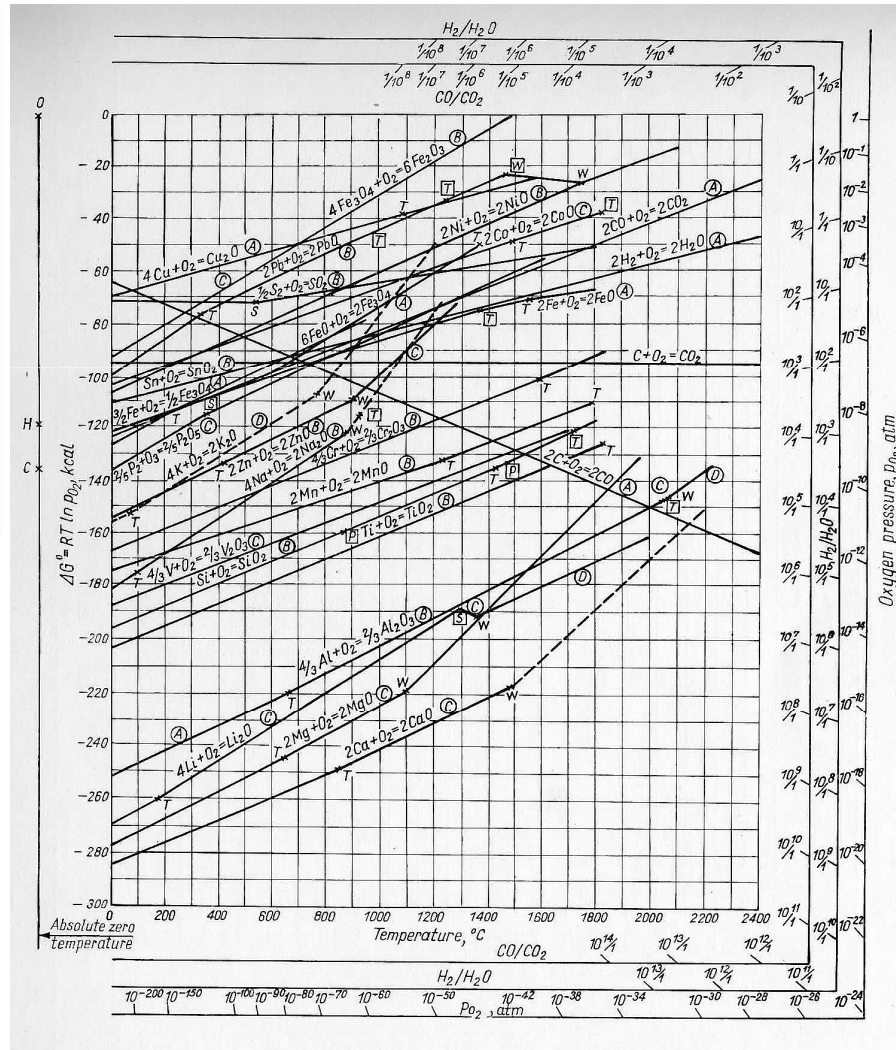
NiO w  $T = 1000\text{ °C}$

odp.:  $p(\text{NiO}) = 10^{-10}\text{ atm}$



# Kolejność tlenków w zgorzelinie wielofazowej

Przykład: określić kolejność występowania tlenków w zgorzelinie powstającej na żelazie, utlenianym w powietrzu w 1000 °C

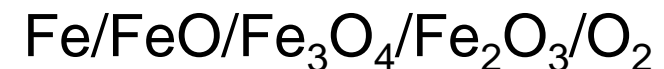


odp.:

$$p(\text{FeO}) \approx 10^{-15} \text{ atm}$$

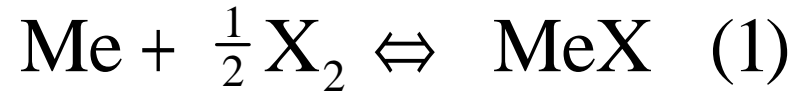
$$p(\text{Fe}_3\text{O}_4) \approx 10^{-12} \text{ atm}$$

$$p(\text{Fe}_2\text{O}_3) \approx 10^{-5} \text{ atm}$$



## Określanie ciśnień dysocjacyjnych

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gdzie: Me – metal; X<sub>2</sub> – utleniacz; MeX – produkt reakcji utleniania (zgorzelina, ang. *scale*)

$$\Delta G = \mu_{\text{MeX}} - \mu_{\text{Me}} - \frac{1}{2} \mu_{\text{X}_2}$$

gdzie: ΔG – zmiana potencjału termodynamicznego reakcji (1);  
μ<sub>i</sub> – potencjał chemiczny danego składnika

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

gdzie: R – stała gazowa; T – temperatura [K]; a<sub>i</sub> – aktywność danego składnika w układzie; μ<sub>i</sub><sup>0</sup> – potencjał chemiczny danego składnika w warunkach standardowych, tj. przy jego aktywności równej jedności

## Określanie ciśnień dysocjacyjnych, c.d.

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W przypadku czystych substancji występujących w stanie stałym:

$$\mu_{\text{Me}} = \mu_{\text{Me}}^0 \quad \text{oraz} \quad \mu_{\text{MeX}} = \mu_{\text{MeX}}^0$$

W przypadku substancji występujących w stanie gazowym:

$$\mu_{\text{X}_2} = \mu_{\text{X}_2}^0 + RT \ln a_{\text{X}_2} = \mu_{\text{X}_2}^0 + RT \ln p_{\text{X}_2}$$

$$\Delta G = \mu_{\text{MeX}} - \mu_{\text{Me}} - \frac{1}{2} \mu_{\text{X}_2} = \mu_{\text{MeX}}^0 - \mu_{\text{Me}}^0 - \frac{1}{2} \mu_{\text{X}_2}^0 - \frac{1}{2} RT \ln p_{\text{X}_2} = \Delta G^0 - \frac{1}{2} RT \ln p_{\text{X}_2}$$

W stanie równowagi termodynamicznej  $\Delta G = 0$ :

$$p_{\text{X}_2} = \exp\left(\frac{2 \cdot \Delta G^0}{RT}\right)$$

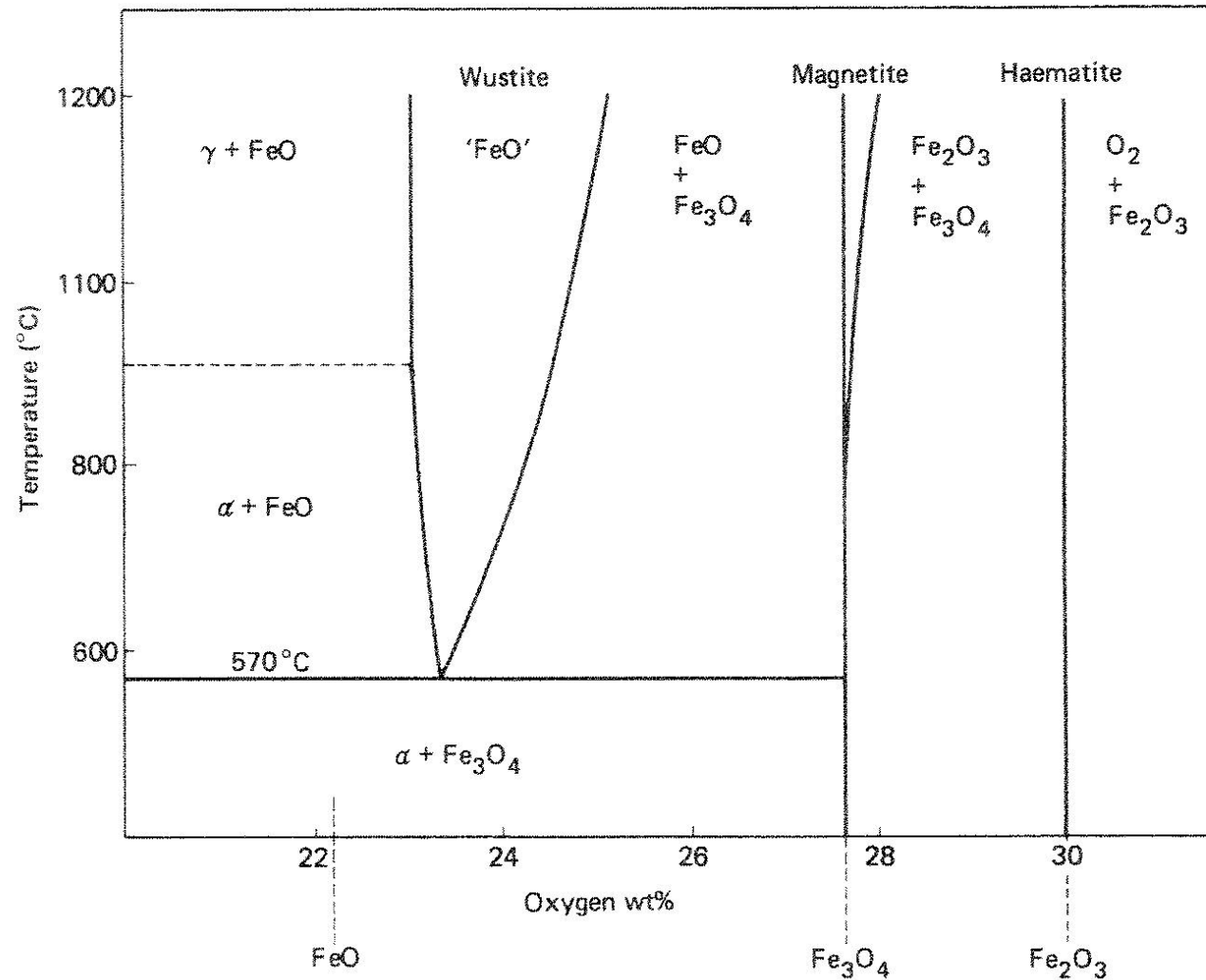
## Kolejność tlenków w zgorzelinie wielofazowej

Przykład: określić kolejność występowania tlenków w zgorzelinie powstającej na żelazie, utlenianym w powietrzu w 1000 °C

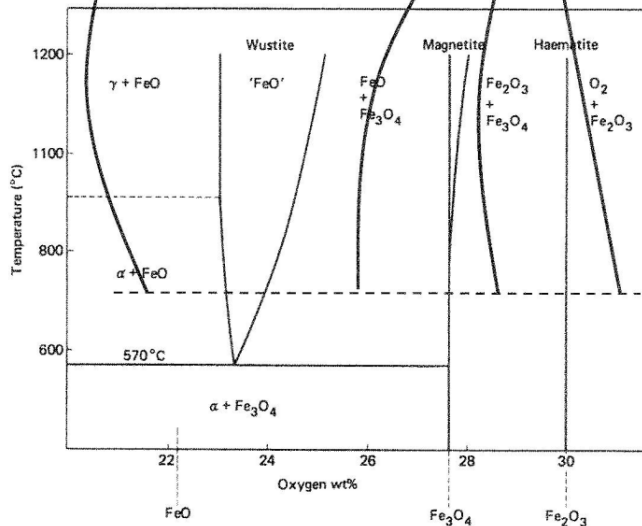
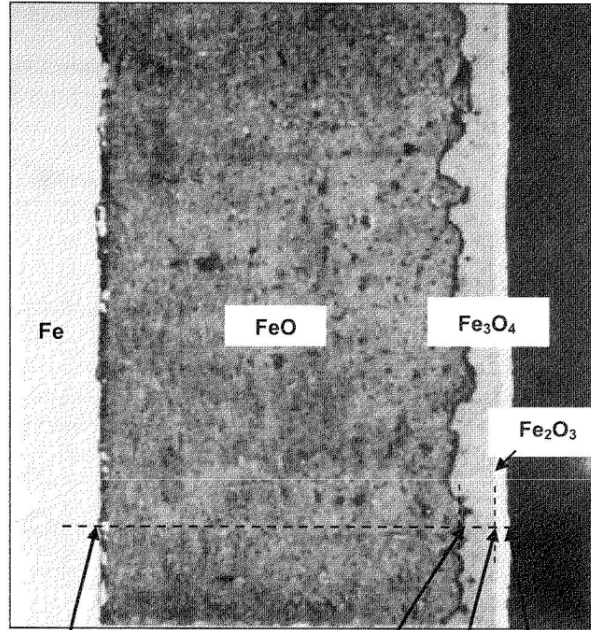




# Diagram fazowy układu Fe-O

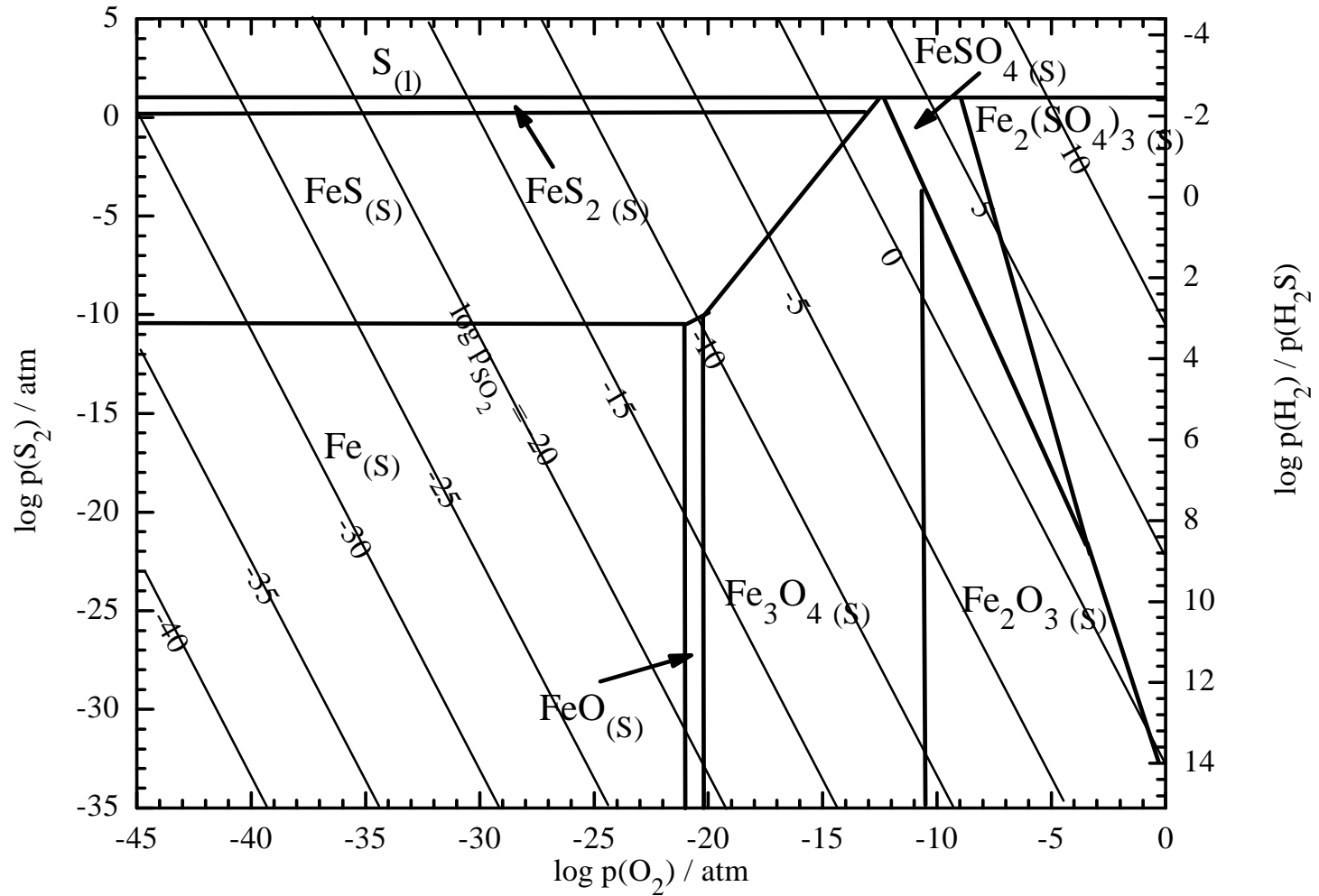


# Przekrój zgorzeliny tlenkowej rosnącej na żelazie w powiązaniu z diagramem fazowym Fe-O

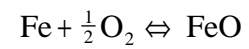
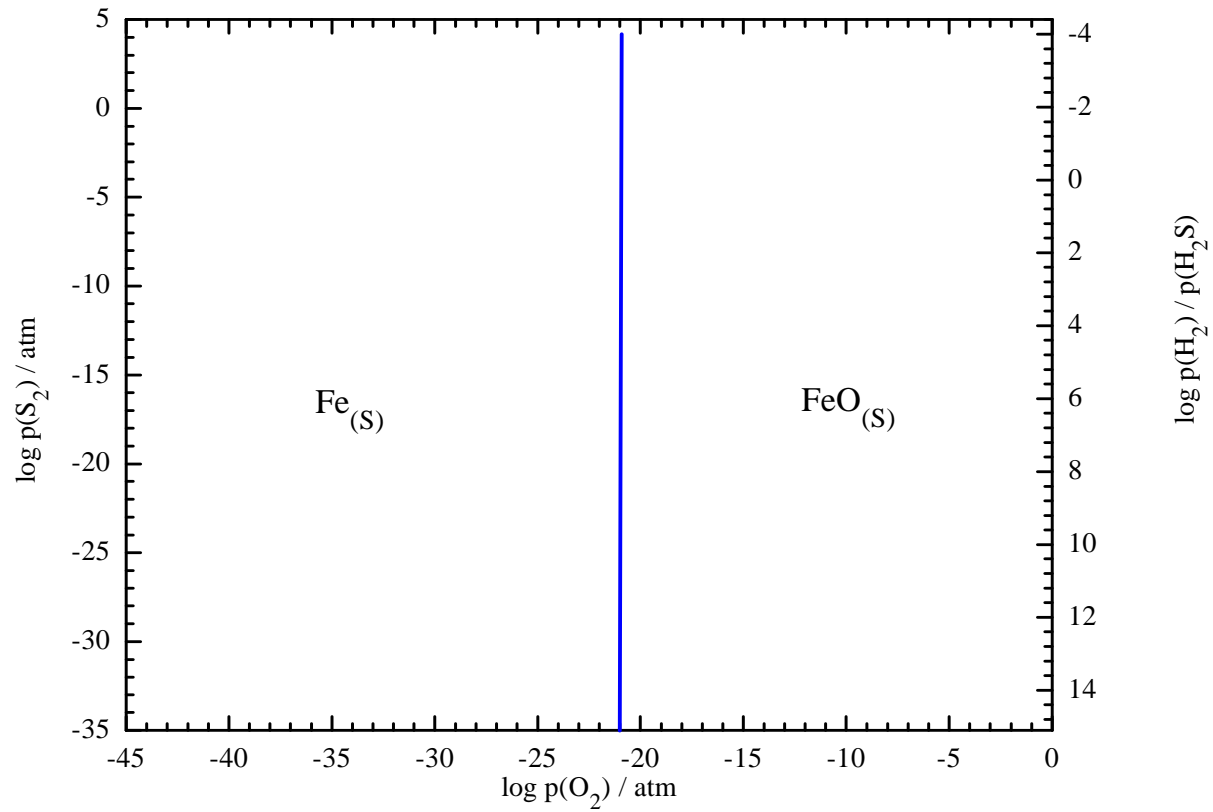


David J. Young, „High temperature oxidation and corrosion of metals”, Elsevier, Sydney 2016.

# Diagramy Kellogg'a

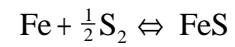
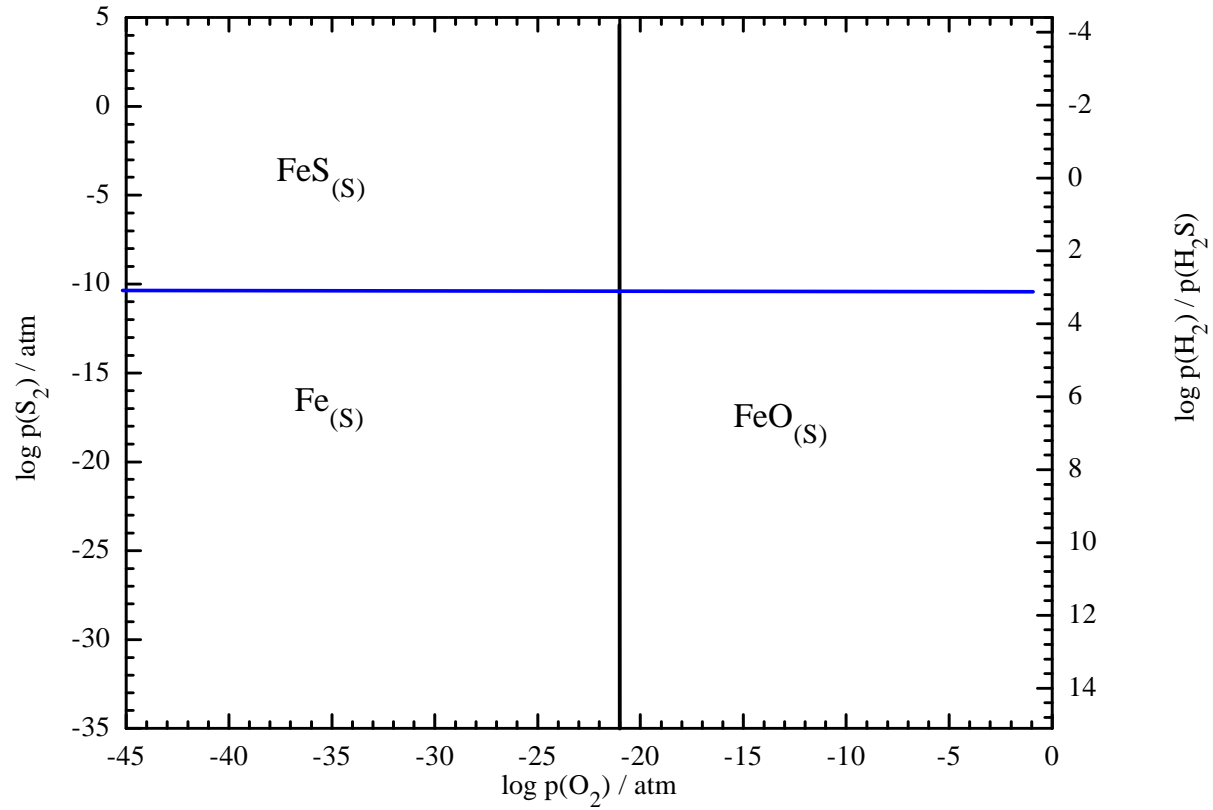


# Diagramy Kellogg'a

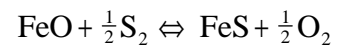
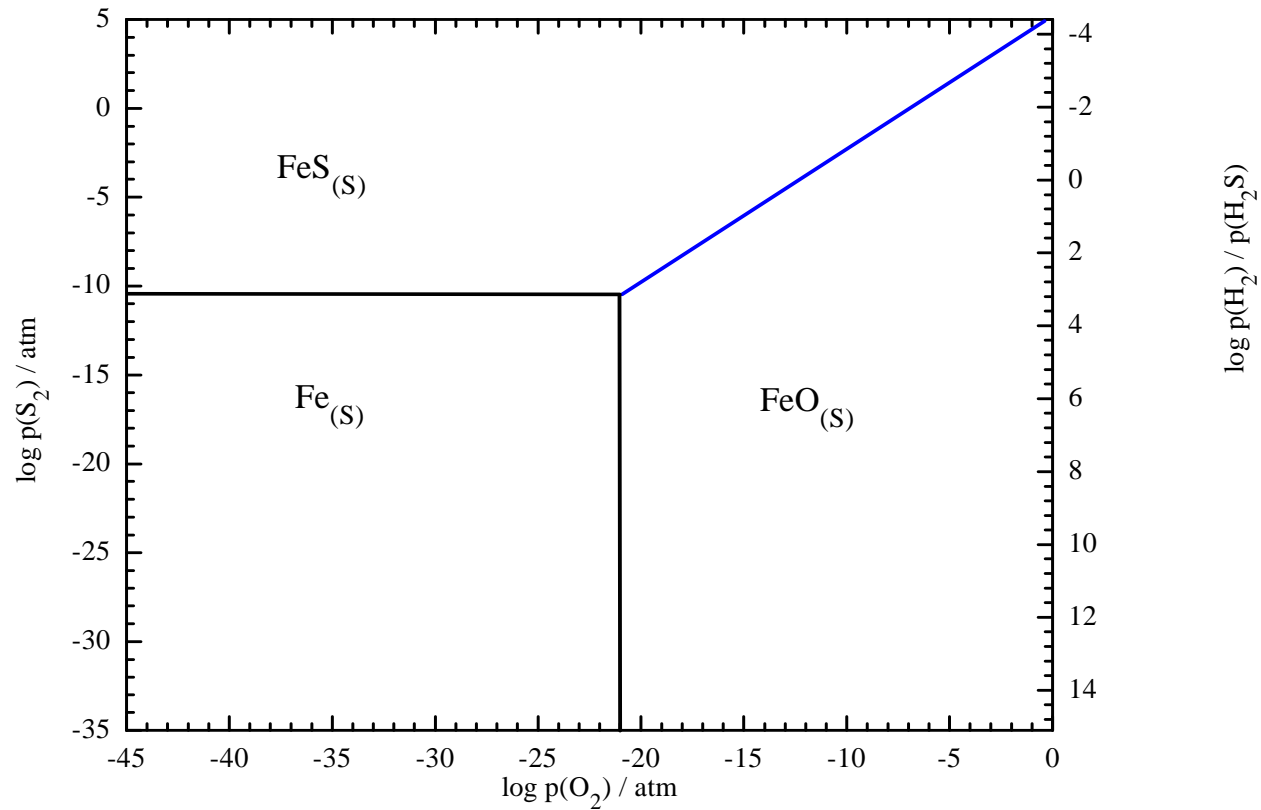




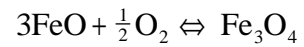
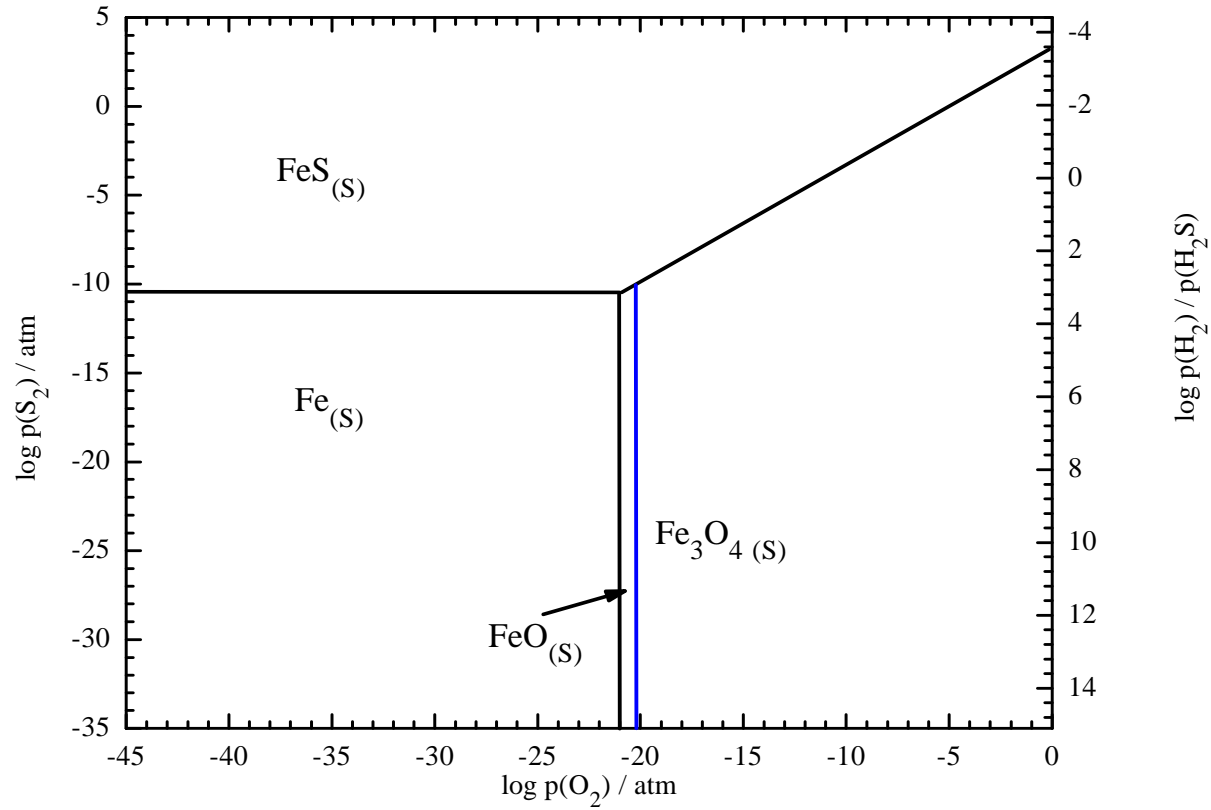
# Diagramy Kellogg'a



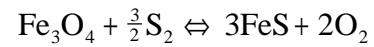
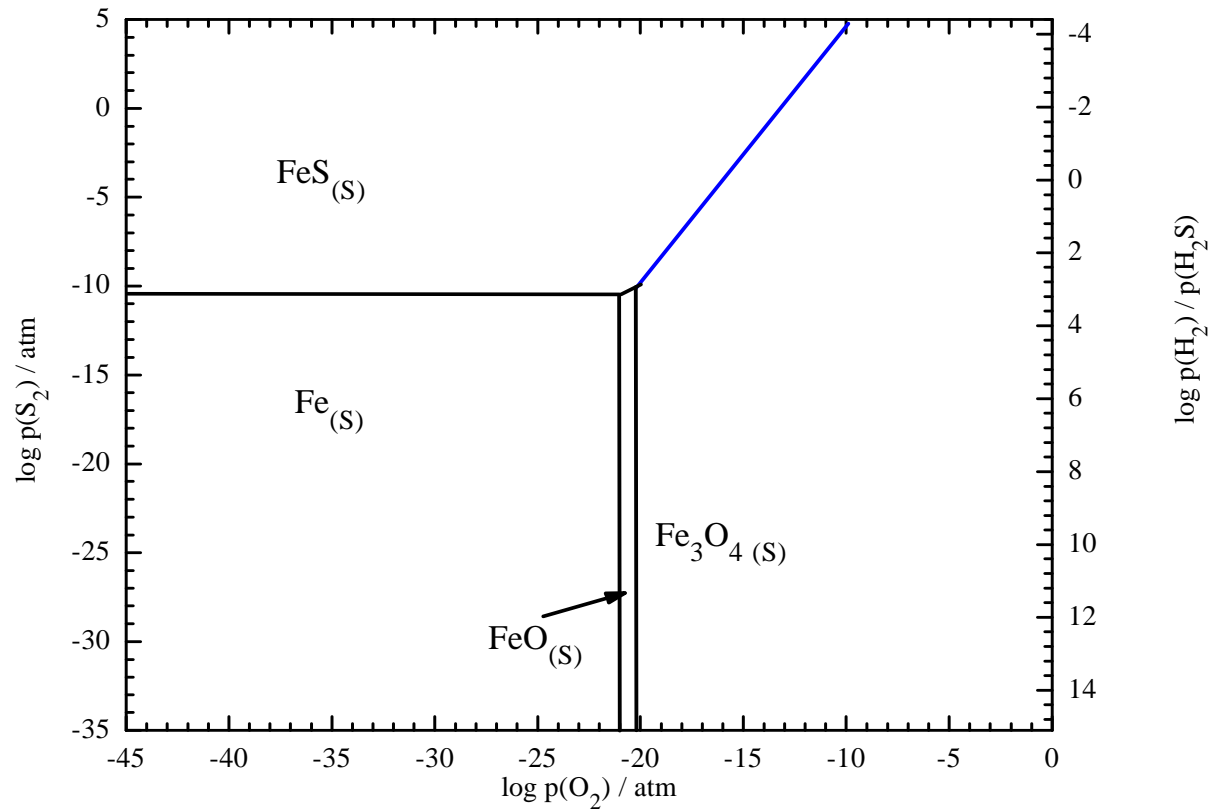
# Diagramy Kellogg'a



# Diagramy Kellogg'a

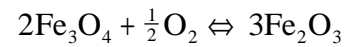
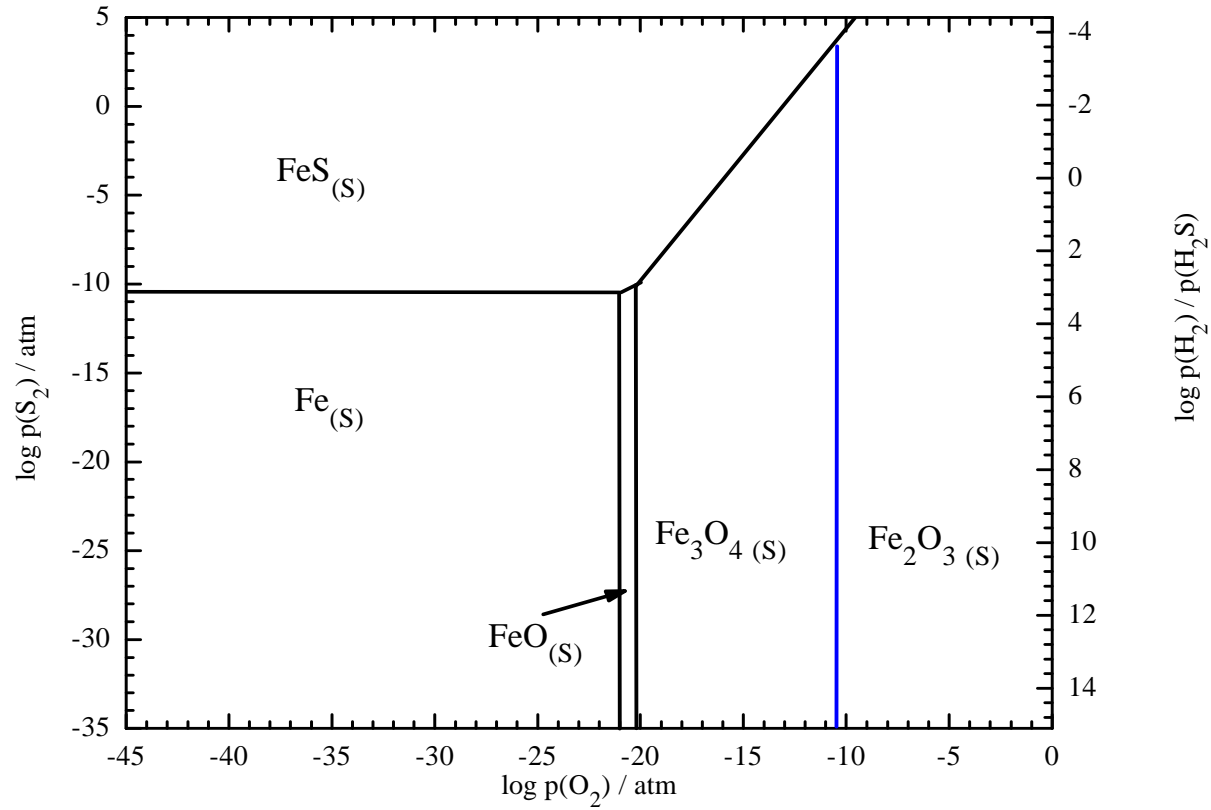


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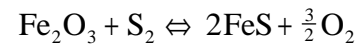
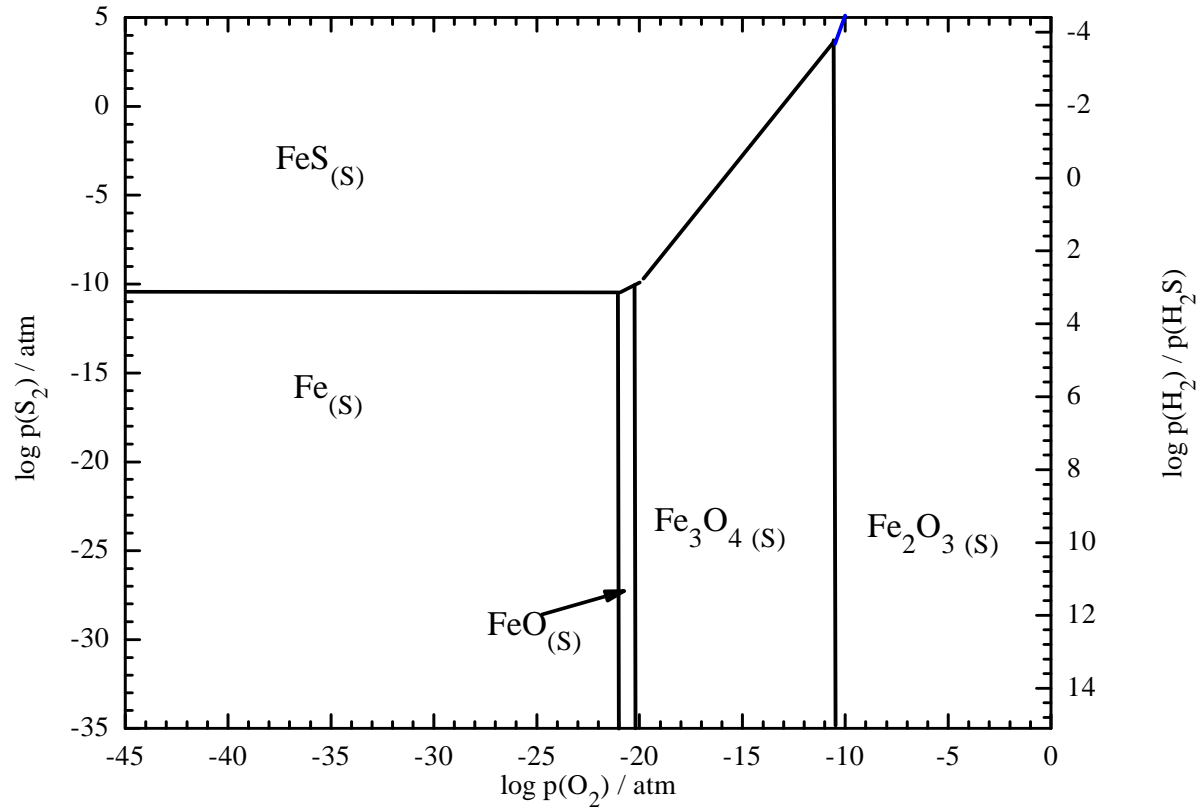




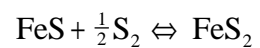
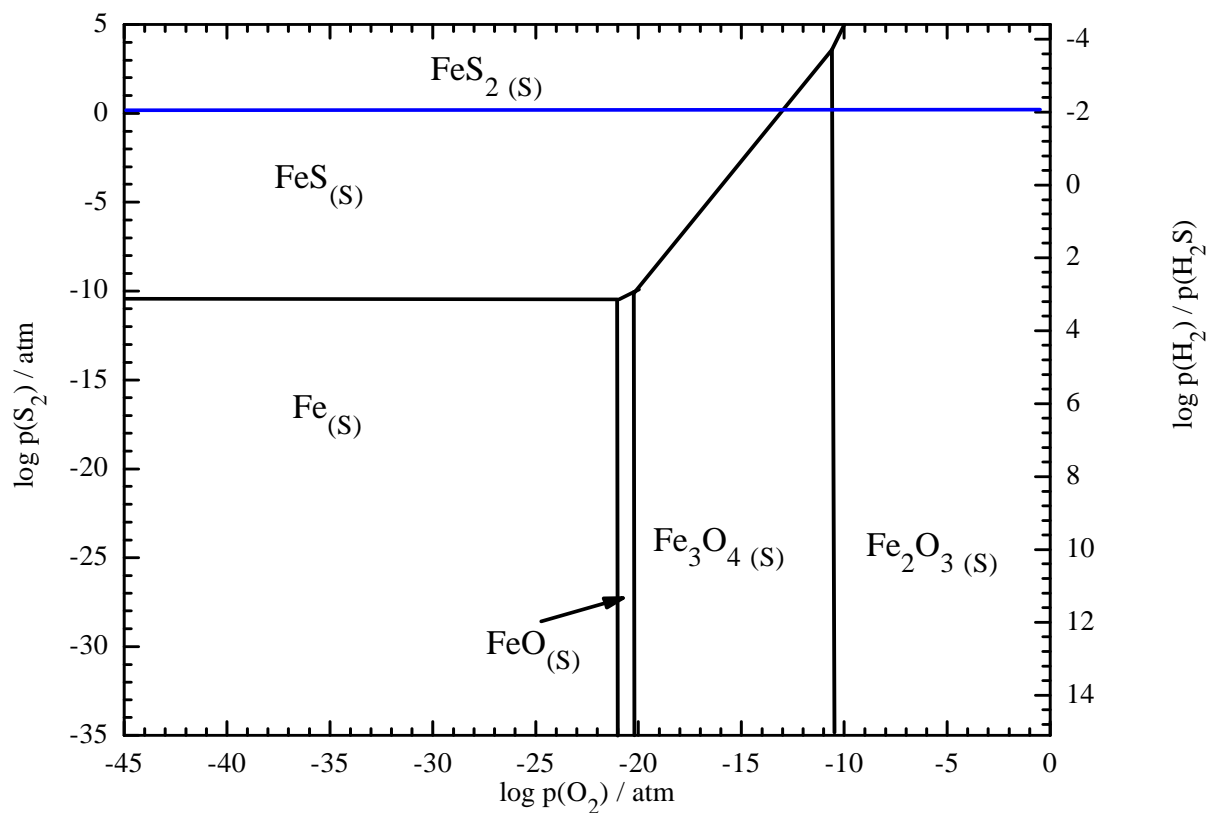
# Diagramy Kellogg'a



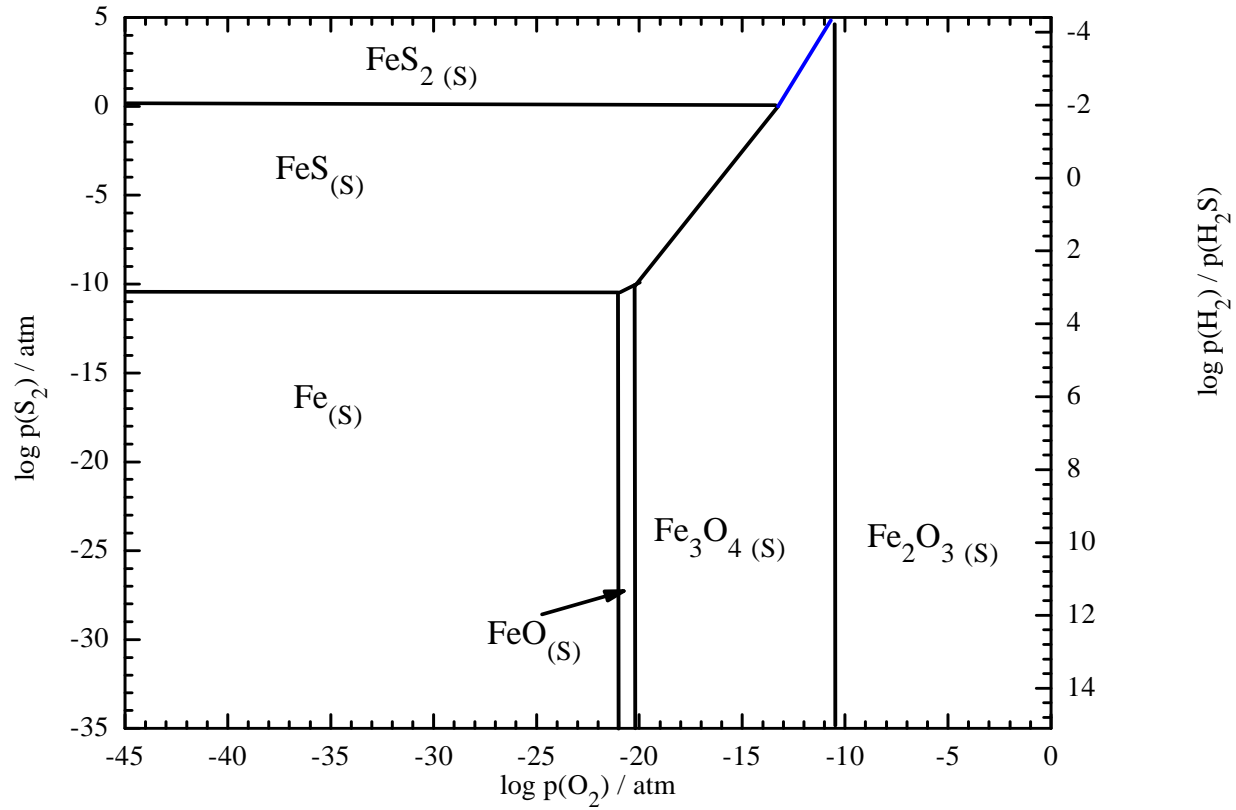
# Diagramy Kellogg'a



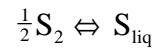
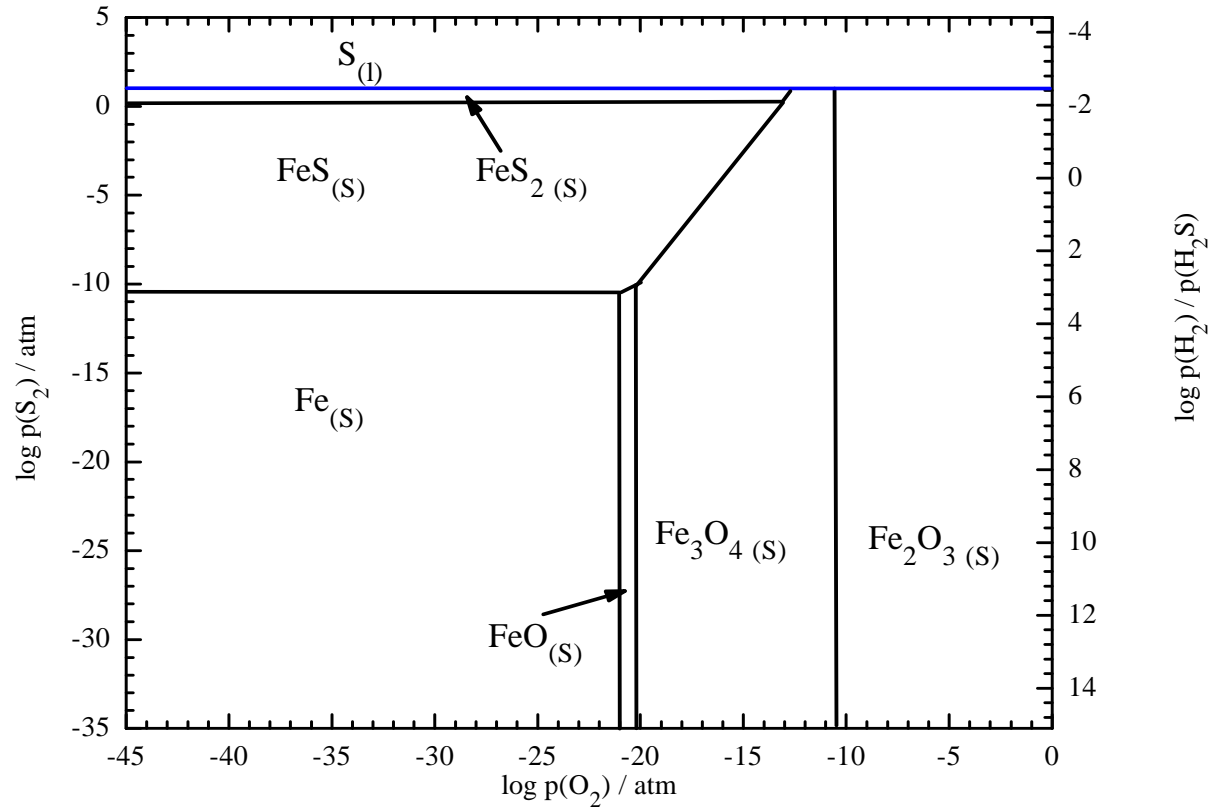
# Diagramy Kellogg'a



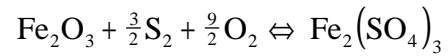
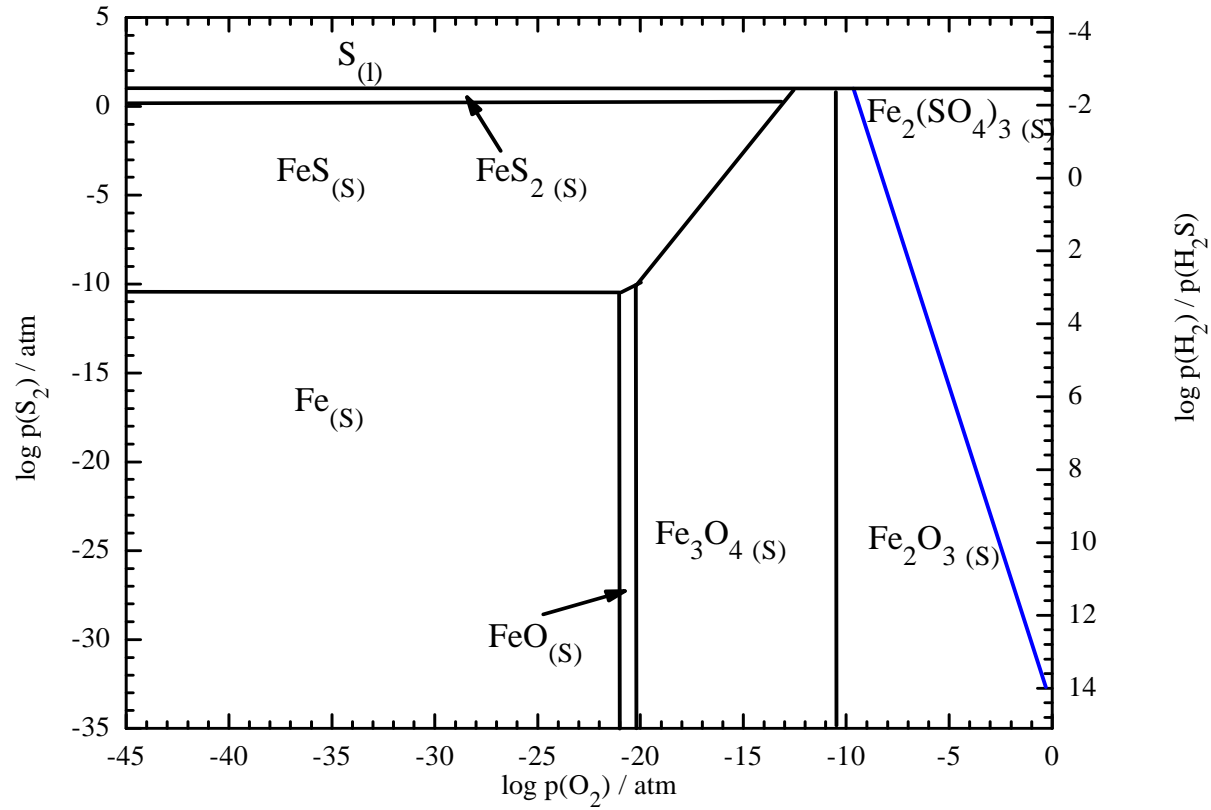
# Diagramy Kellogg'a



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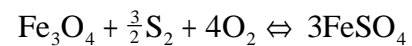
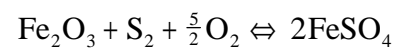
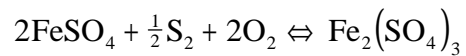
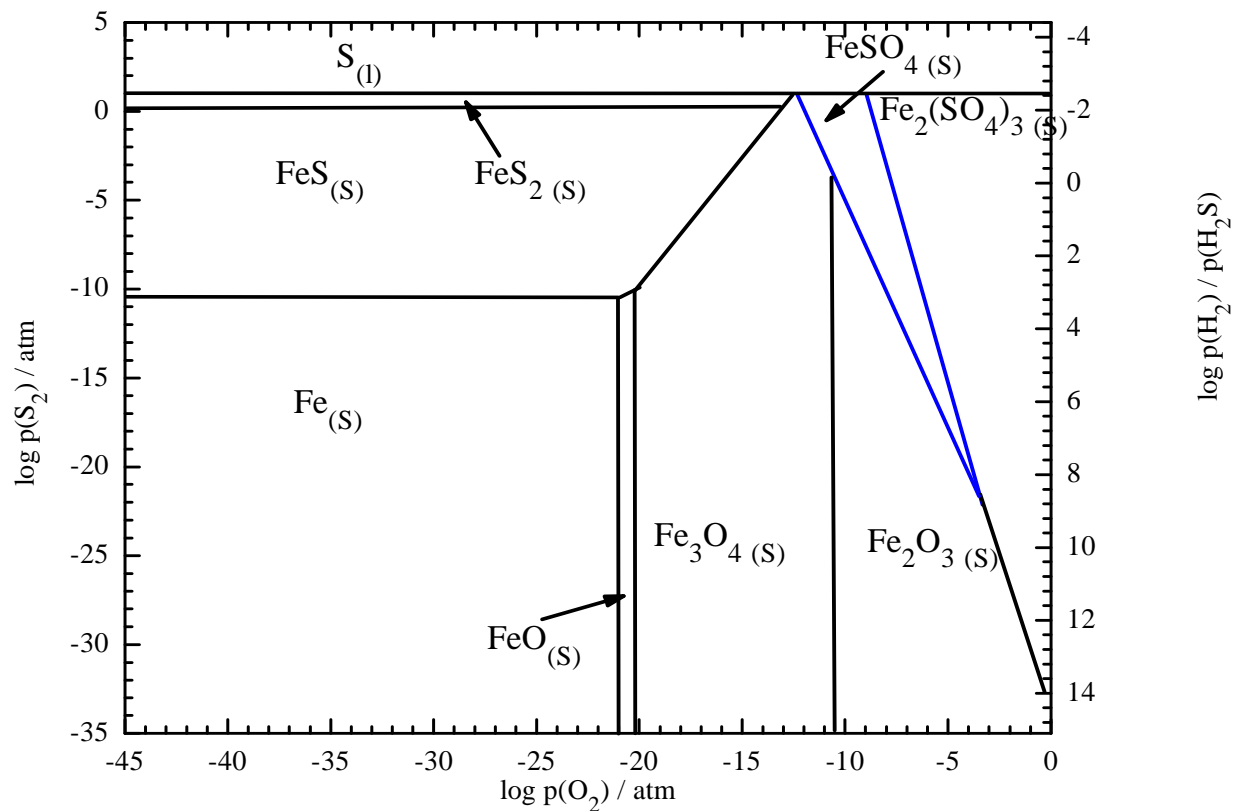


# Diagramy Kellogg'a

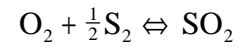
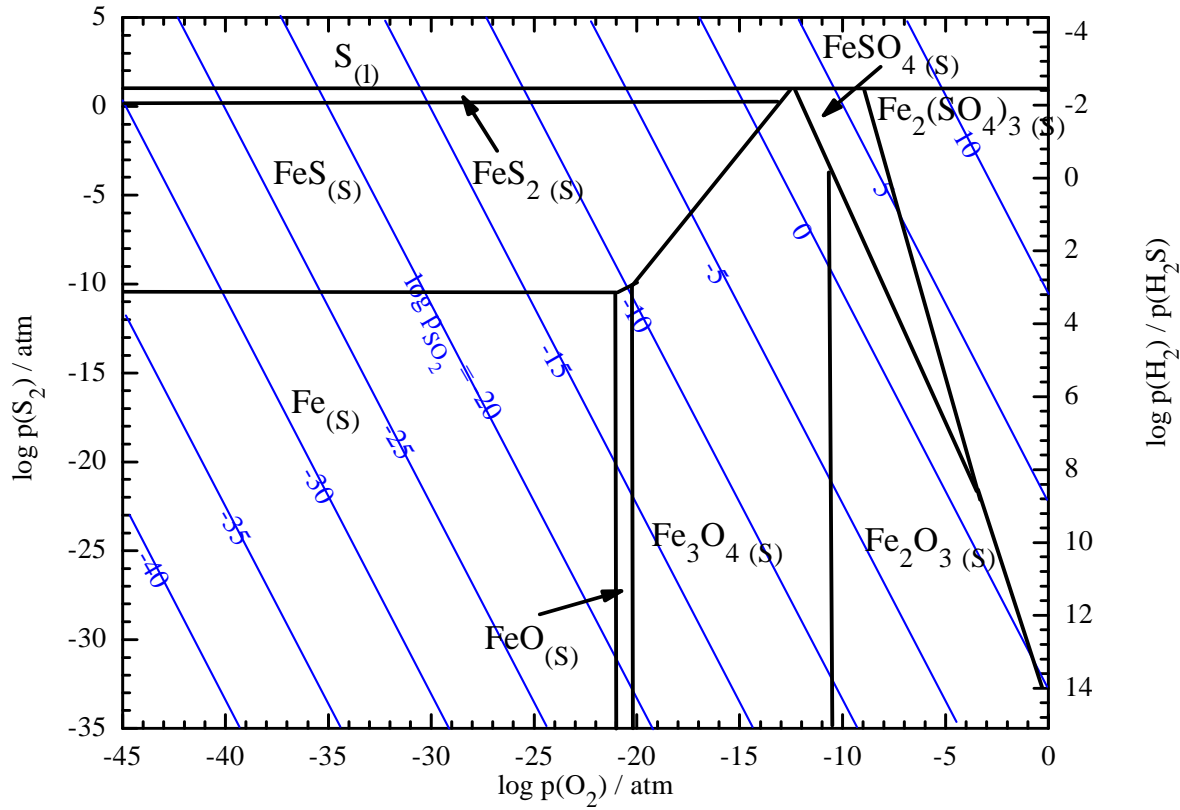




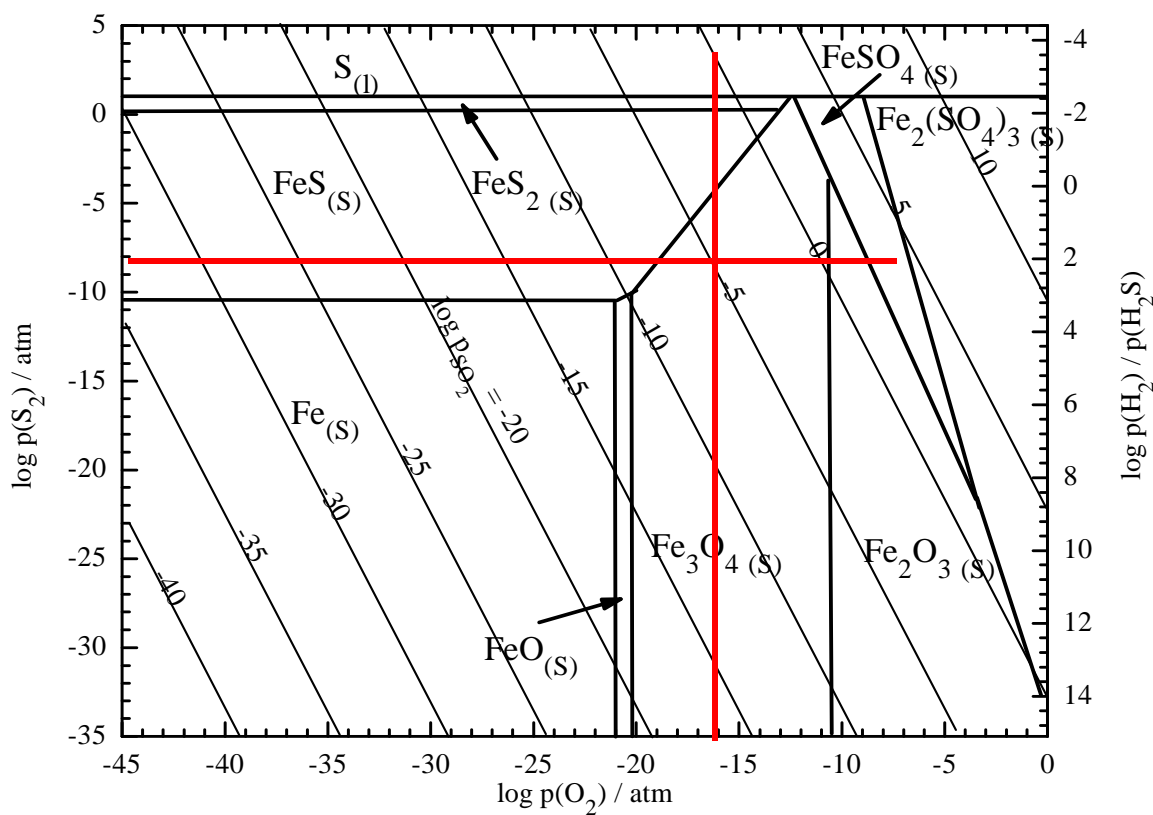
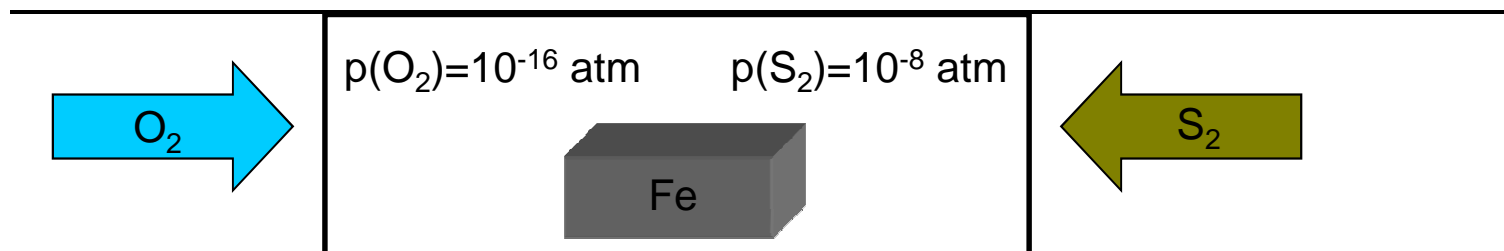
# Diagramy Kellogg'a



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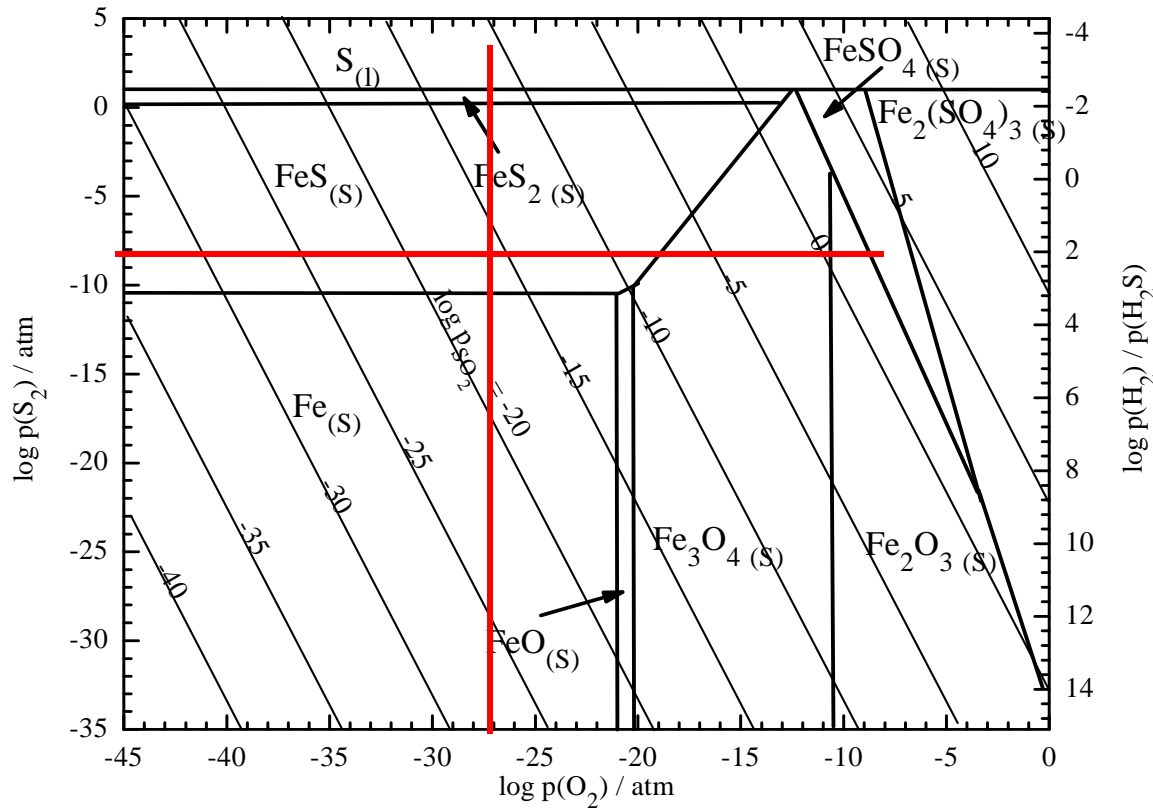
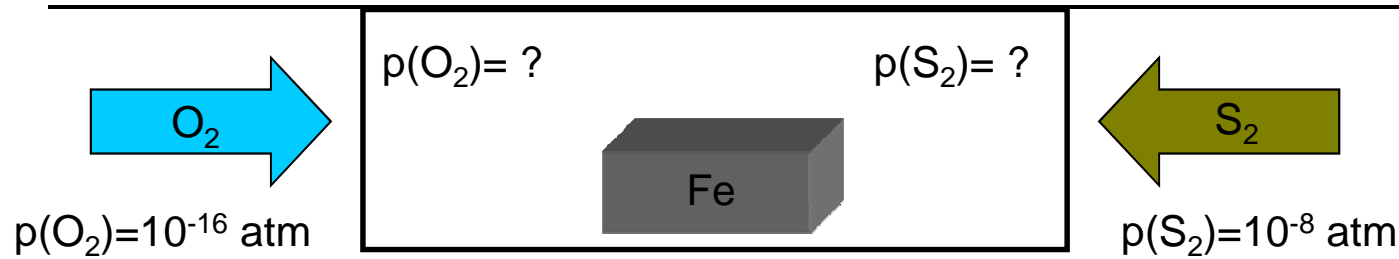


# Diagramy Kellogg'a



odp.:  $\text{Fe} \longrightarrow \text{Fe}_3\text{O}_4$

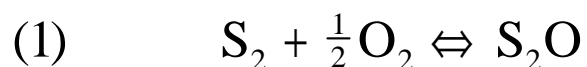
# Diagramy Kellogg'a



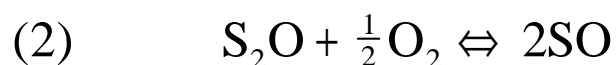
odp.:  $\text{Fe} \longrightarrow \text{FeS}$

# Ciśnienia cząstkowe gazów w mieszaninach

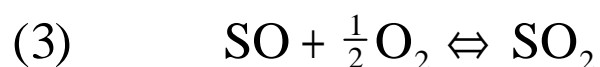
## Układ tlen - siarka



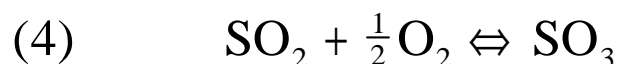
$$p_{\text{O}_2} = \left( \frac{p_{\text{S}_2\text{O}}}{p_{\text{S}_2}} \right)^2 \cdot \exp\left( \frac{2\Delta G_1^0}{RT} \right)$$



$$p_{\text{O}_2} = \left( \frac{p_{\text{SO}}^2}{p_{\text{S}_2\text{O}}} \right)^2 \cdot \exp\left( \frac{2\Delta G_2^0}{RT} \right)$$



$$p_{\text{O}_2} = \left( \frac{p_{\text{SO}_2}}{p_{\text{SO}}} \right)^2 \cdot \exp\left( \frac{2\Delta G_3^0}{RT} \right)$$



$$p_{\text{O}_2} = \left( \frac{p_{\text{SO}_3}}{p_{\text{SO}_2}} \right)^2 \cdot \exp\left( \frac{2\Delta G_4^0}{RT} \right)$$

$$N_{\text{S}} = 2n_{\text{S}_2} + 2n_{\text{S}_2\text{O}} + n_{\text{SO}} + n_{\text{SO}_2} + n_{\text{SO}_3}$$

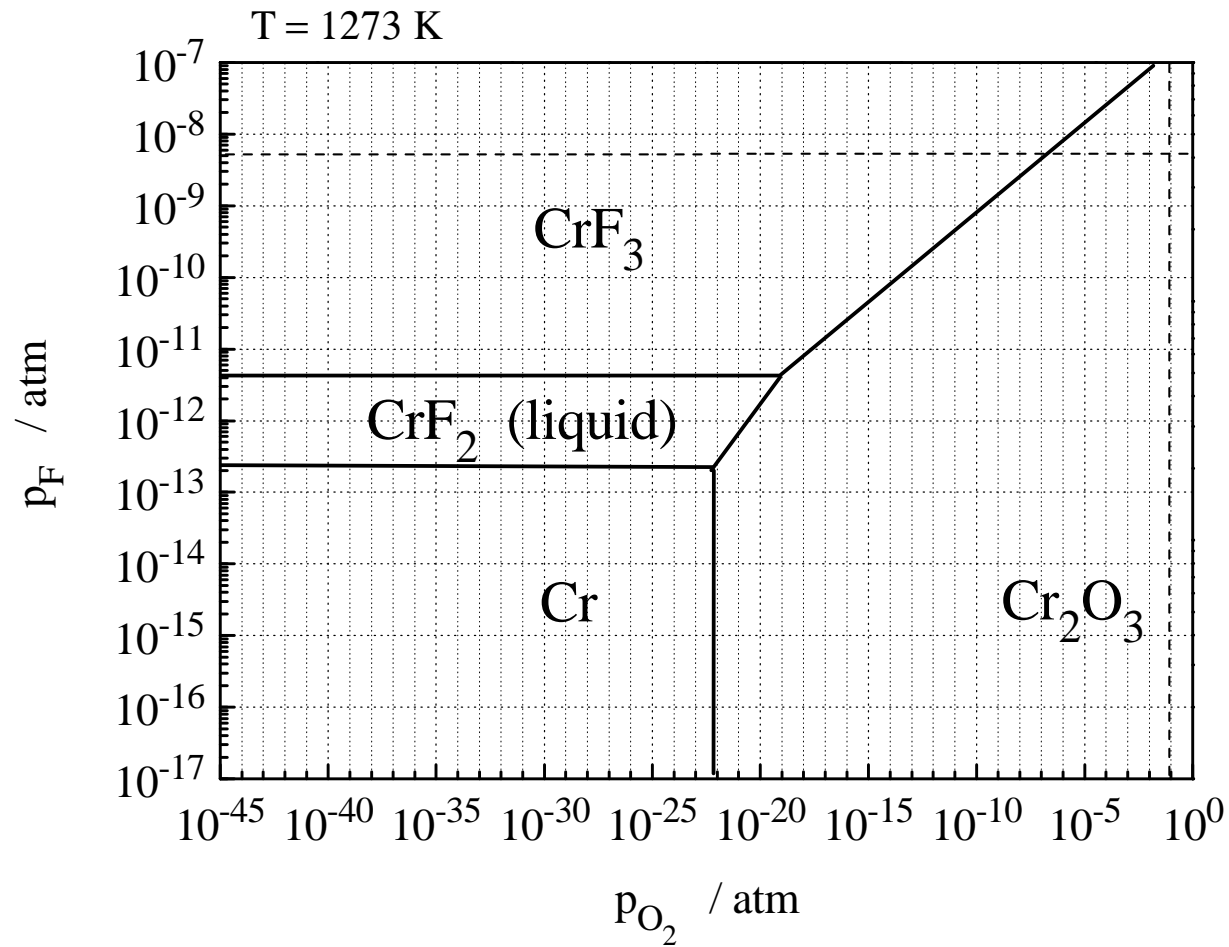
$$N_{\text{O}_2} = n_{\text{O}_2} + \frac{1}{2} n_{\text{S}_2\text{O}} + \frac{1}{2} n_{\text{SO}} + n_{\text{SO}_2} + \frac{3}{2} n_{\text{SO}_3}$$

$N_{\text{S}}$  i  $N_{\text{O}_2}$  oznaczają całkowite ilości moli S i  $\text{O}_2$  obecnych w systemie,  $n_{\text{S}_2}$ ,  $n_{\text{S}_2\text{O}}$ ,  $n_{\text{SO}}$ ,  $n_{\text{SO}_2}$ ,  $n_{\text{SO}_3}$ ,  $n_{\text{O}_2}$  – ilość moli poszczególnych gazów w stanie równowagi termodynamicznej.

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

gdzie  $n_i$  jest ilością moli składnika  $i$ ,  $m$  – liczbą wszystkich składników w układzie, natomiast  $p_{\text{tot}}$  oznacza całkowite ciśnienie mieszaniny gazowej.

# Diagramy Kellogg'a





# Diagramy Kellogg'a

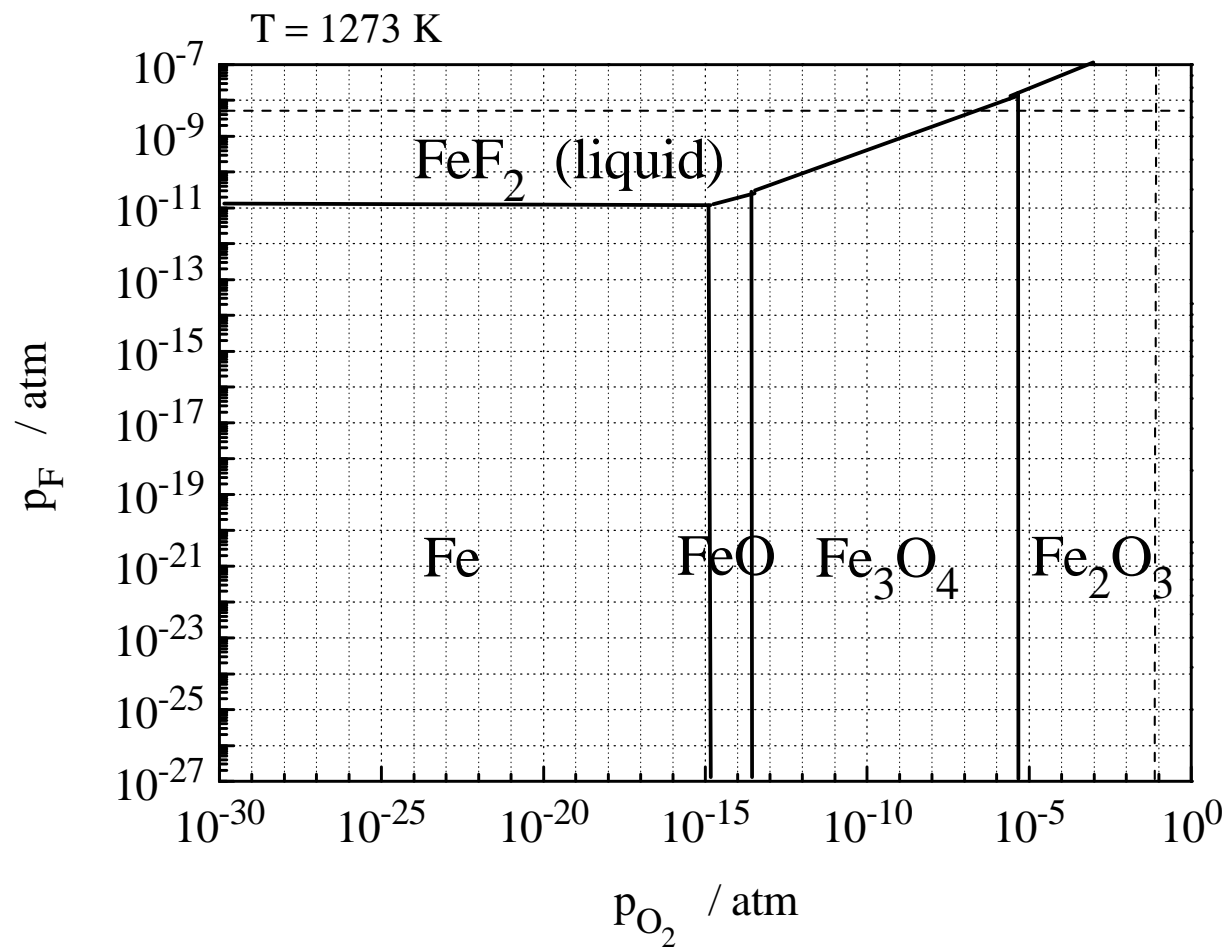
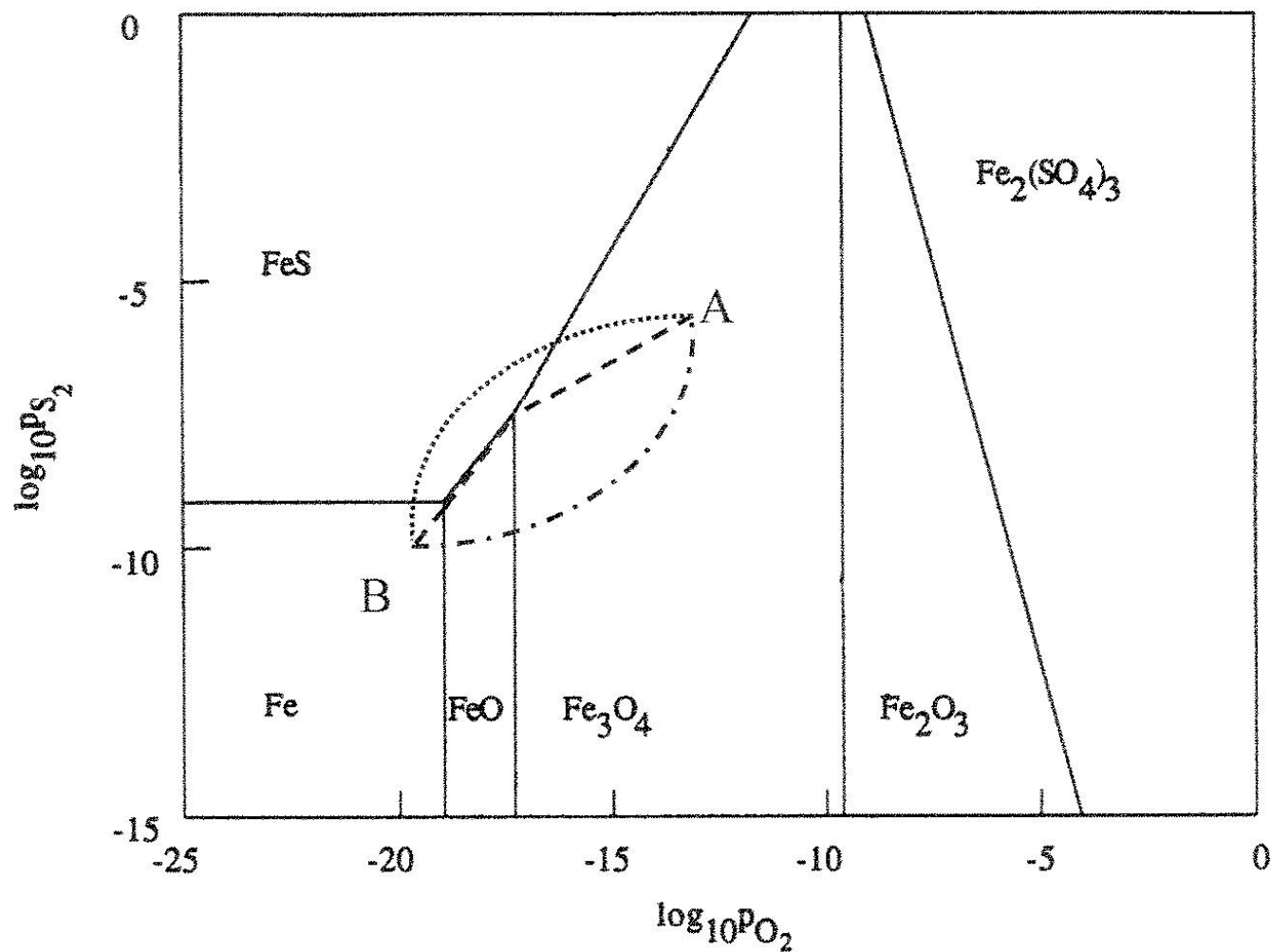
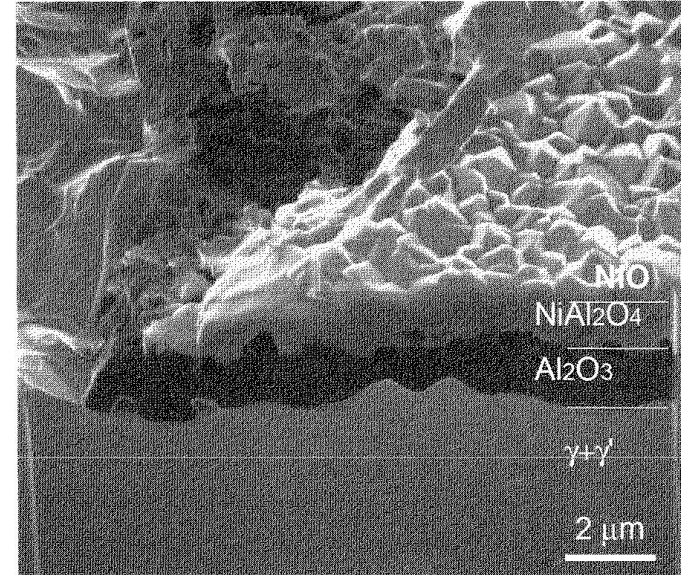
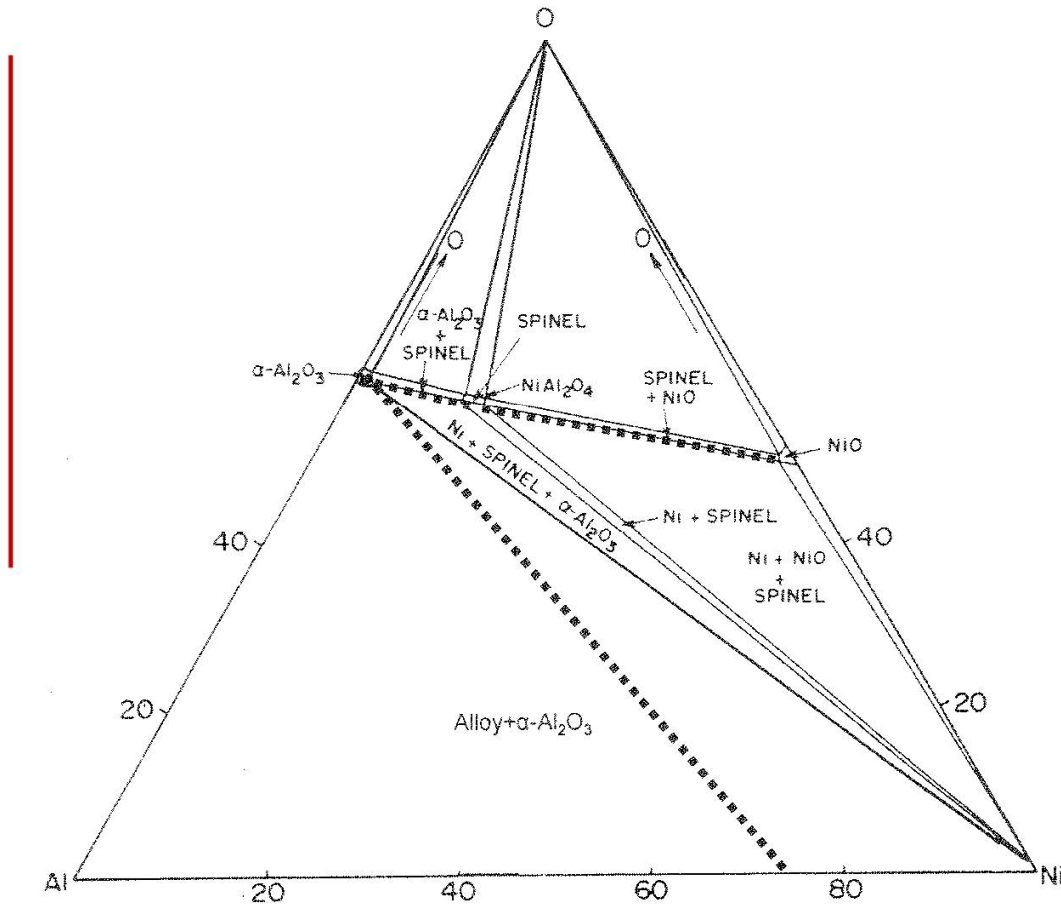


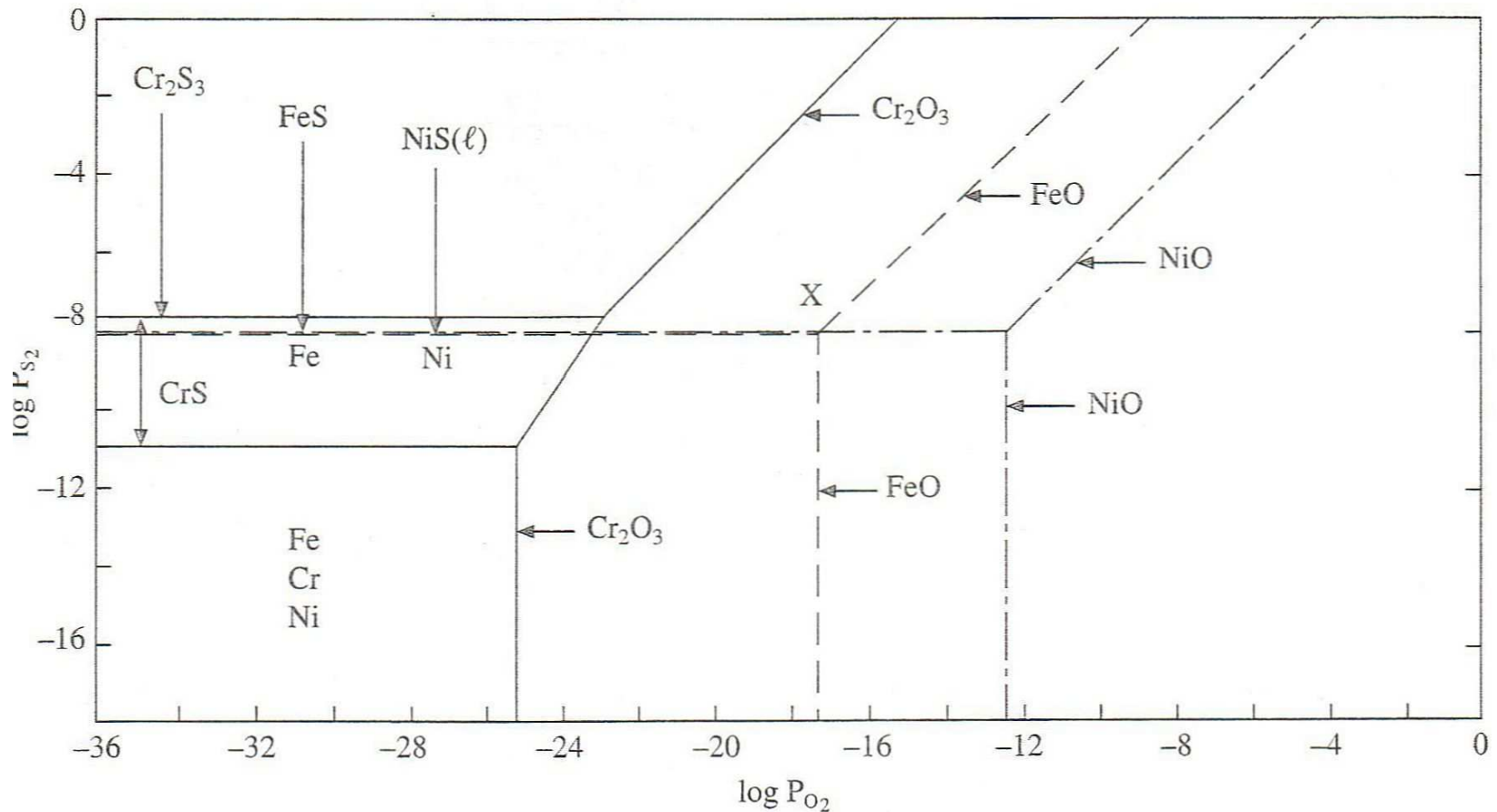
Diagram Kellogg'a dla układu Fe-O-S w 800 °C, ilustrujący trzy możliwe drogi dyfuzji dla reakcji z gazem o składzie A



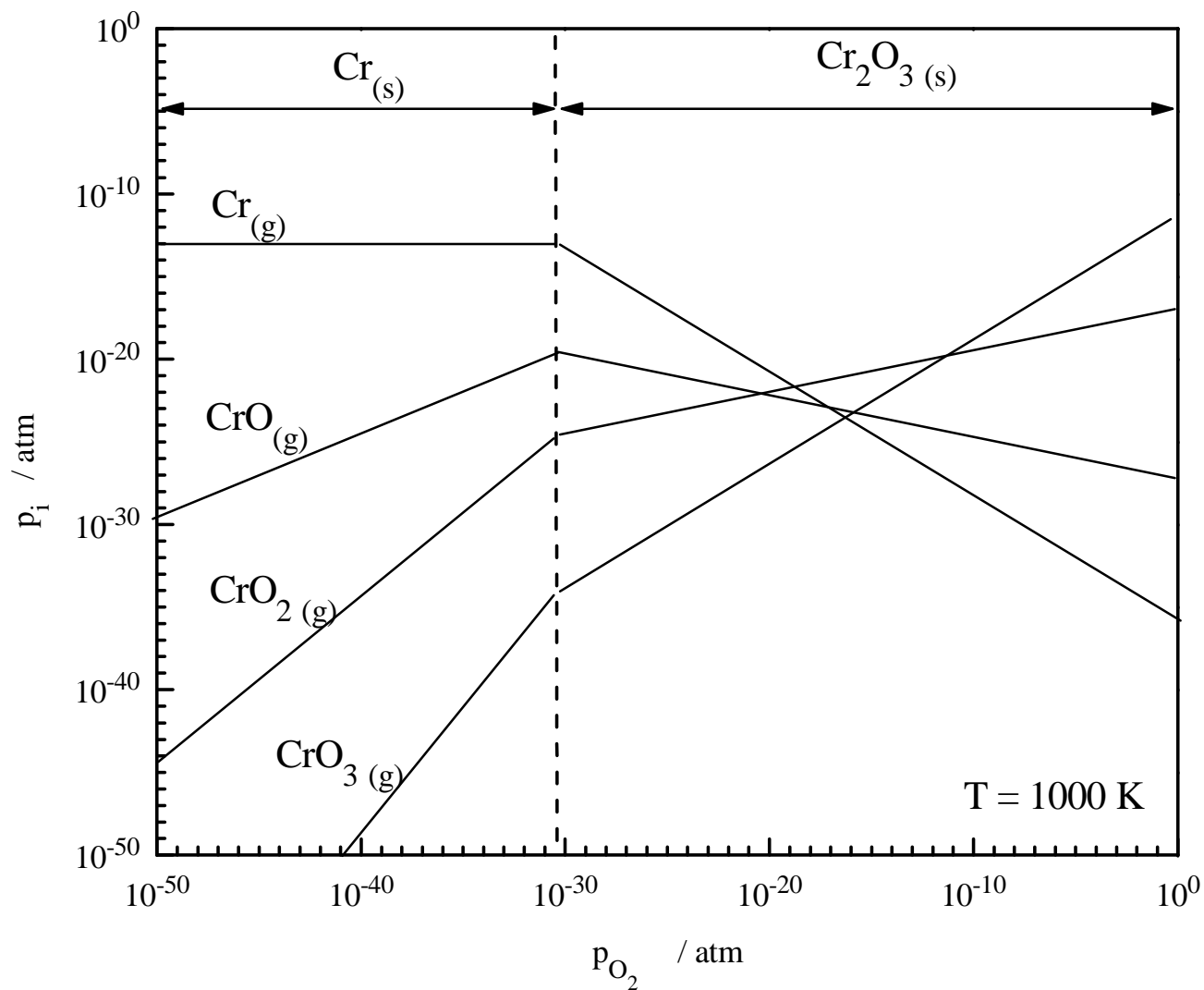
# Diagram fazowy układu Al-Ni-O w 1000 °C i przekrój zgorzeliny tlenkowej powstającej na Ni-22Al



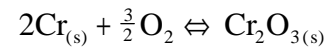
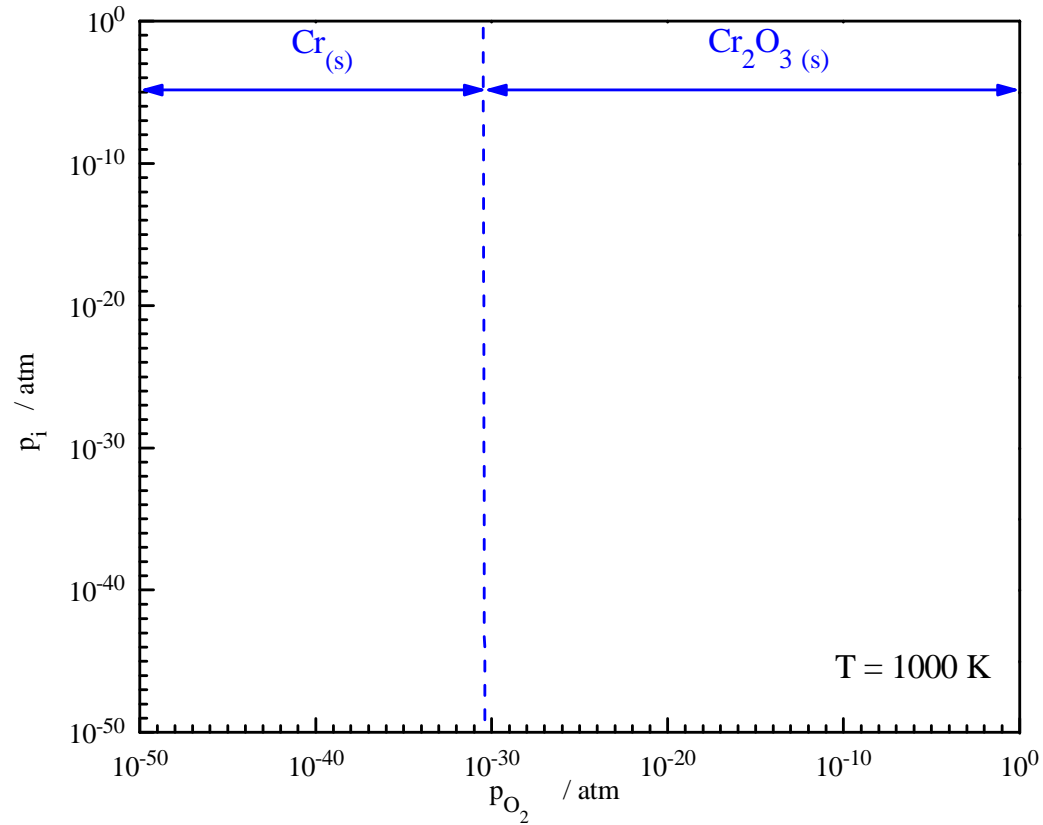
# Diagram Kellog'a układu (Fe-Cr-Ni)-O-S w 870 °C



# Ciśnienia lotnych tlenków



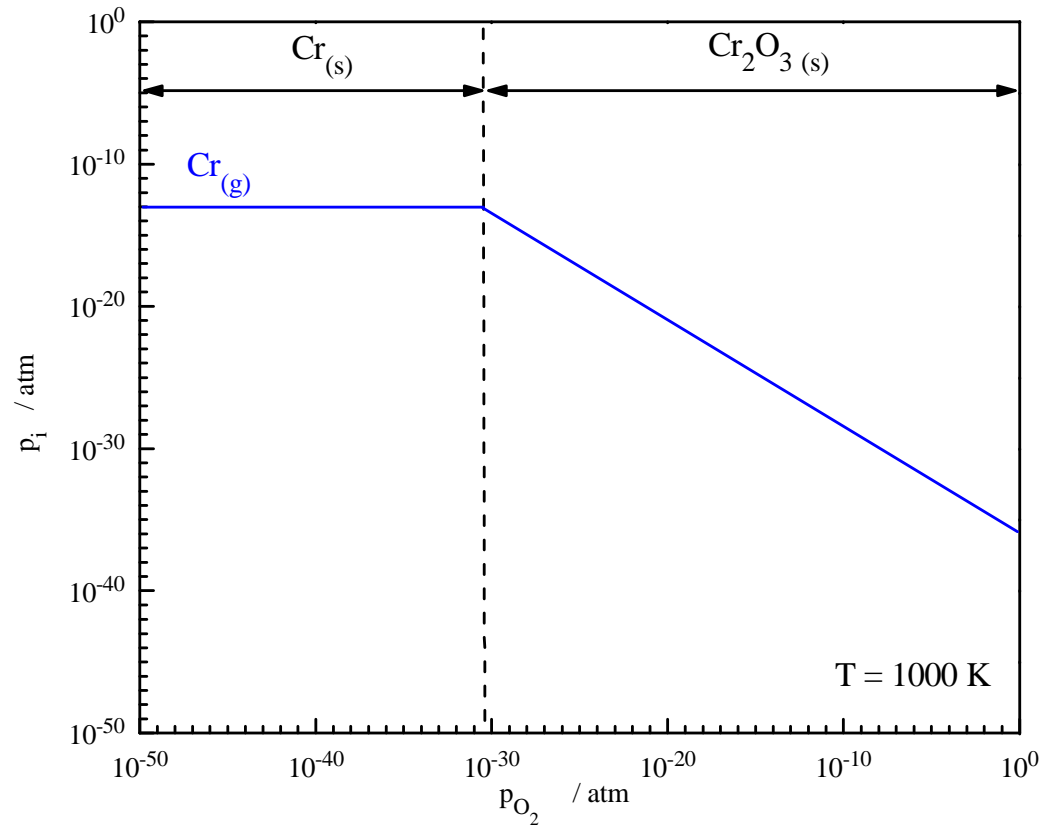
# Ciśnienia lotnych tlenków



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



# Ciśnienia lotnych tlenków

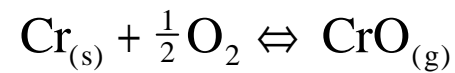
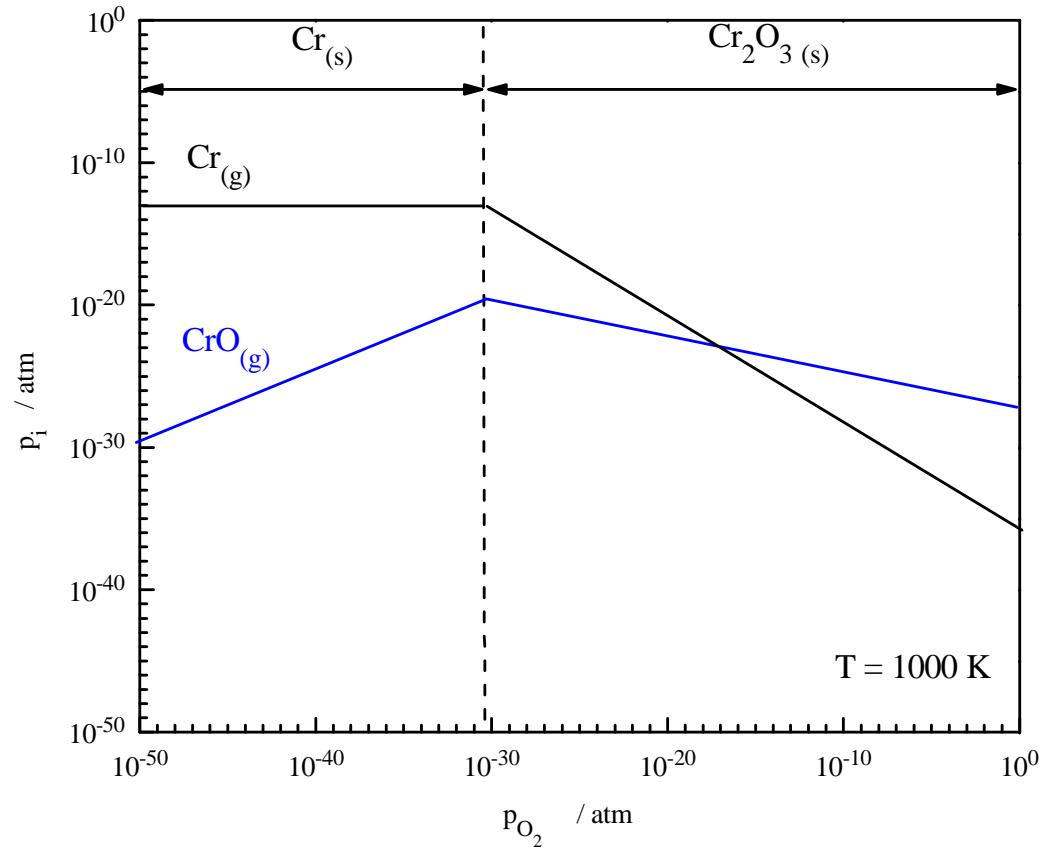


$$p_{Cr_{(g)}} = \exp\left(-\frac{\Delta G^0}{RT}\right)$$



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

# Ciśnienia lotnych tlenków

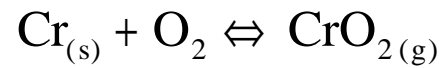
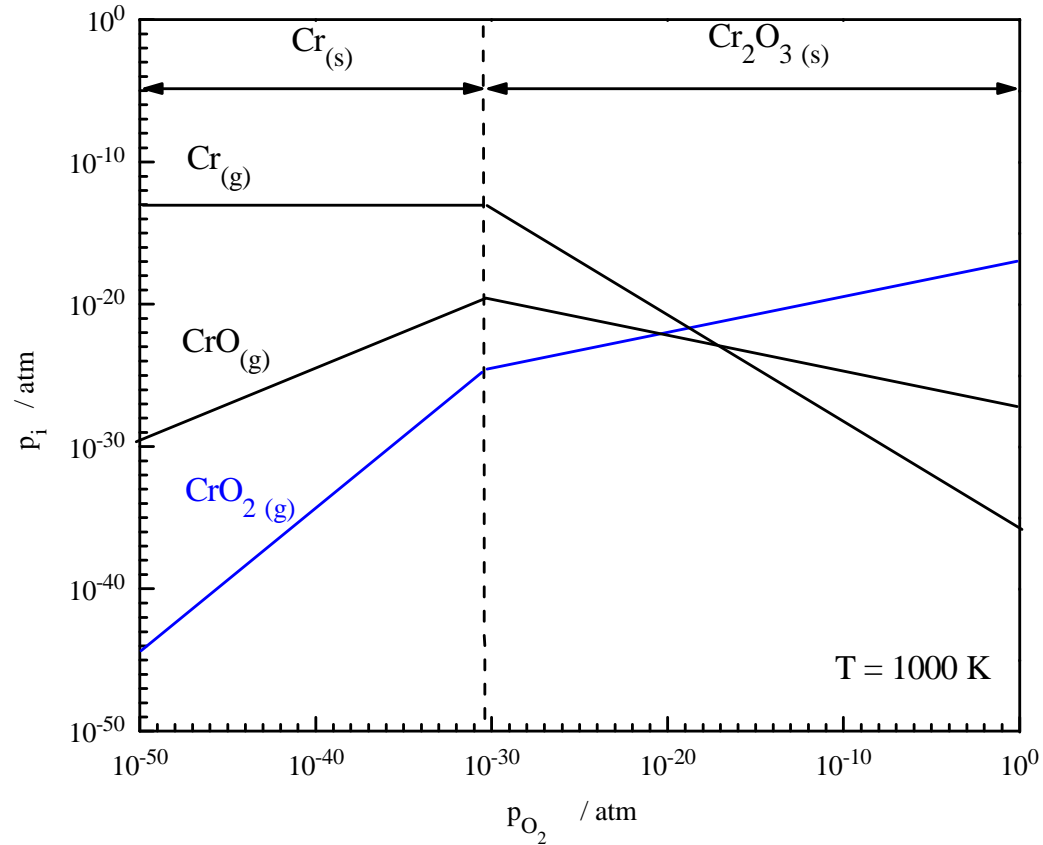


$$p_{CrO_{(g)}} = p_{O_2}^{\frac{1}{2}} \exp\left(-\frac{\Delta G^0}{RT}\right)$$

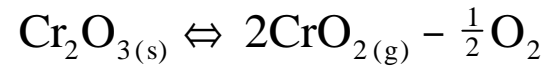


$$p_{CrO_{(g)}} = p_{O_2}^{-\frac{1}{4}} \exp\left(-\frac{\Delta G^0}{2RT}\right)$$

# Ciśnienia lotnych tlenków

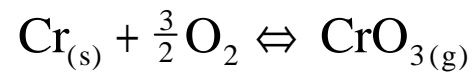
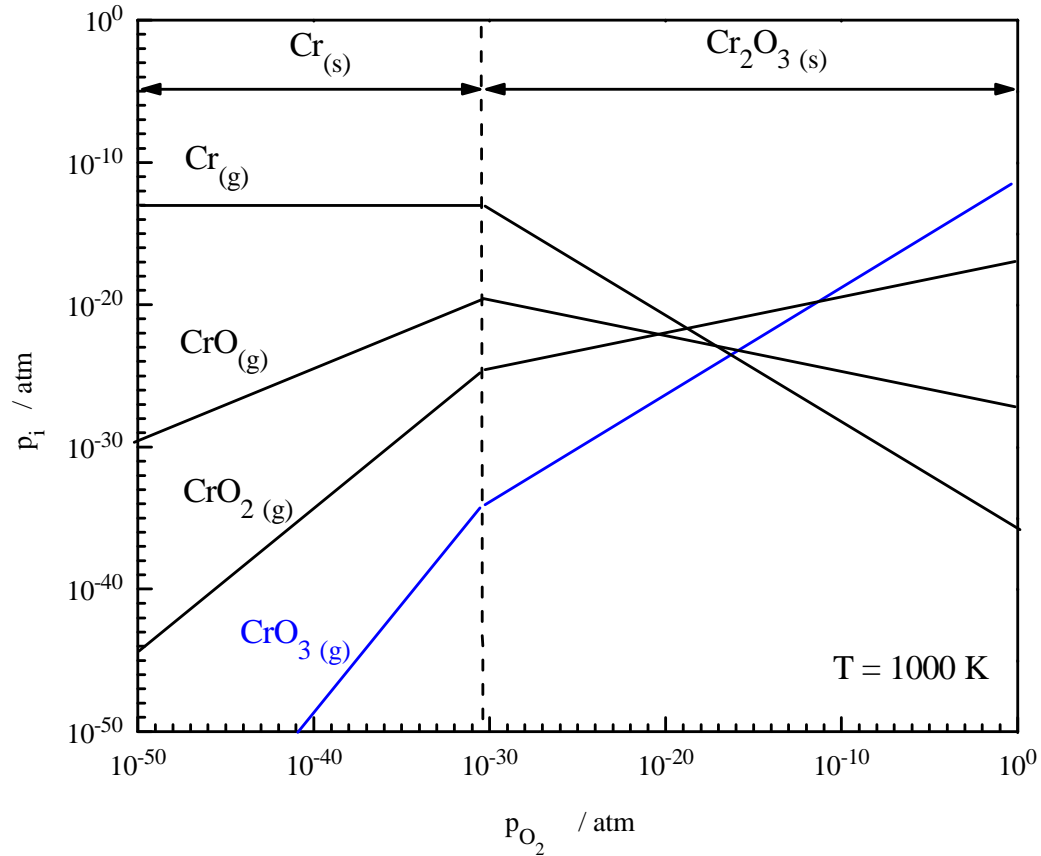


$$p_{\text{CrO}_{2(g)}} = p_{\text{O}_2} \exp\left(-\frac{\Delta G^0}{RT}\right)$$



$$p_{\text{CrO}_{2(g)}} = p_{\text{O}_2}^{\frac{1}{4}} \exp\left(-\frac{\Delta G^0}{2RT}\right)$$

# Ciśnienia lotnych tlenków

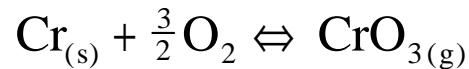
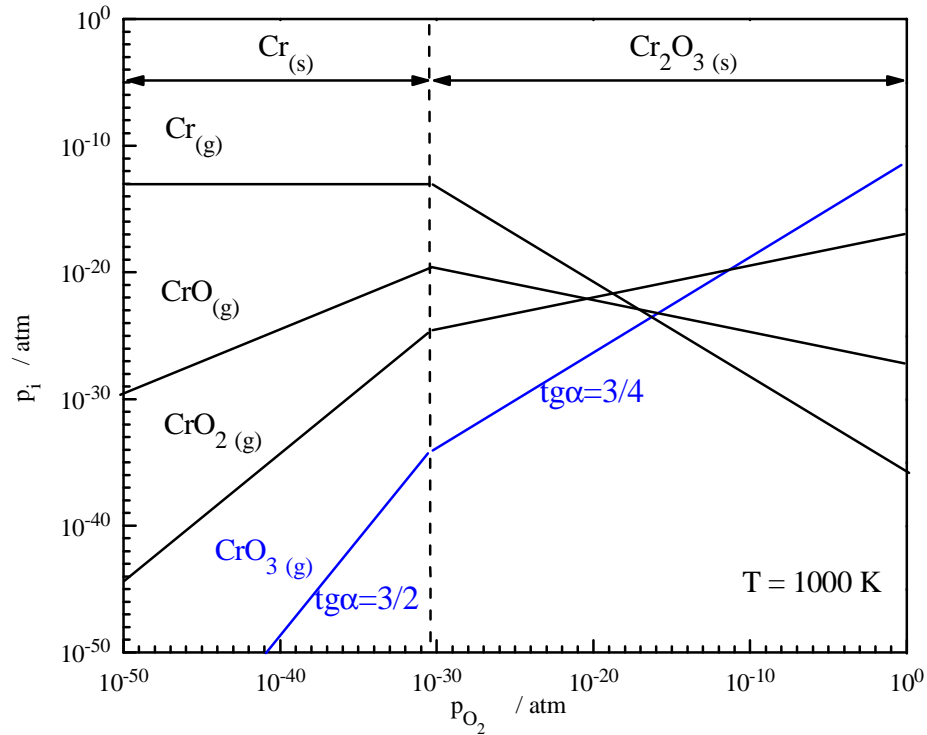


$$p_{CrO_3(g)} = p_{O_2}^{\frac{3}{2}} \exp\left(-\frac{\Delta G^0}{RT}\right)$$



$$p_{CrO_3(g)} = p_{O_2}^{\frac{3}{4}} \exp\left(-\frac{\Delta G^0}{2RT}\right)$$

# Ciśnienia lotnych tlenków



$$p_{\text{CrO}_{3(g)}} = p_{\text{O}_2}^{\frac{3}{2}} \exp\left(-\frac{\Delta G^0}{RT}\right) = p_{\text{O}_2}^{\frac{3}{2}} \cdot \text{const}$$

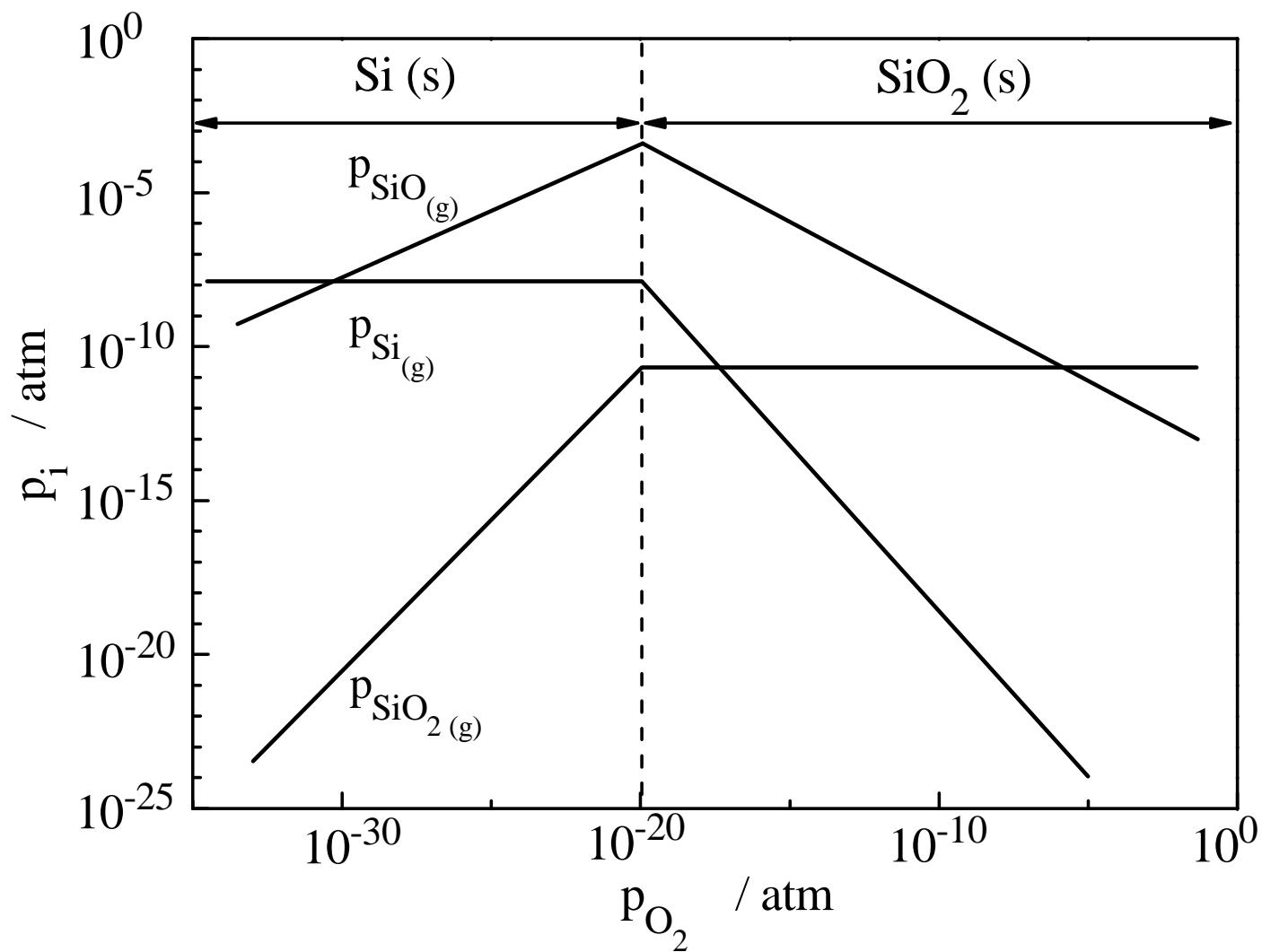
$$\log p_{\text{CrO}_{3(g)}} = \frac{3}{2} \log p_{\text{O}_2} + \log(\text{const})$$



$$p_{\text{CrO}_{3(g)}} = p_{\text{O}_2}^{\frac{3}{4}} \exp\left(-\frac{\Delta G^0}{2RT}\right) = p_{\text{O}_2}^{\frac{3}{4}} \cdot \text{const}$$

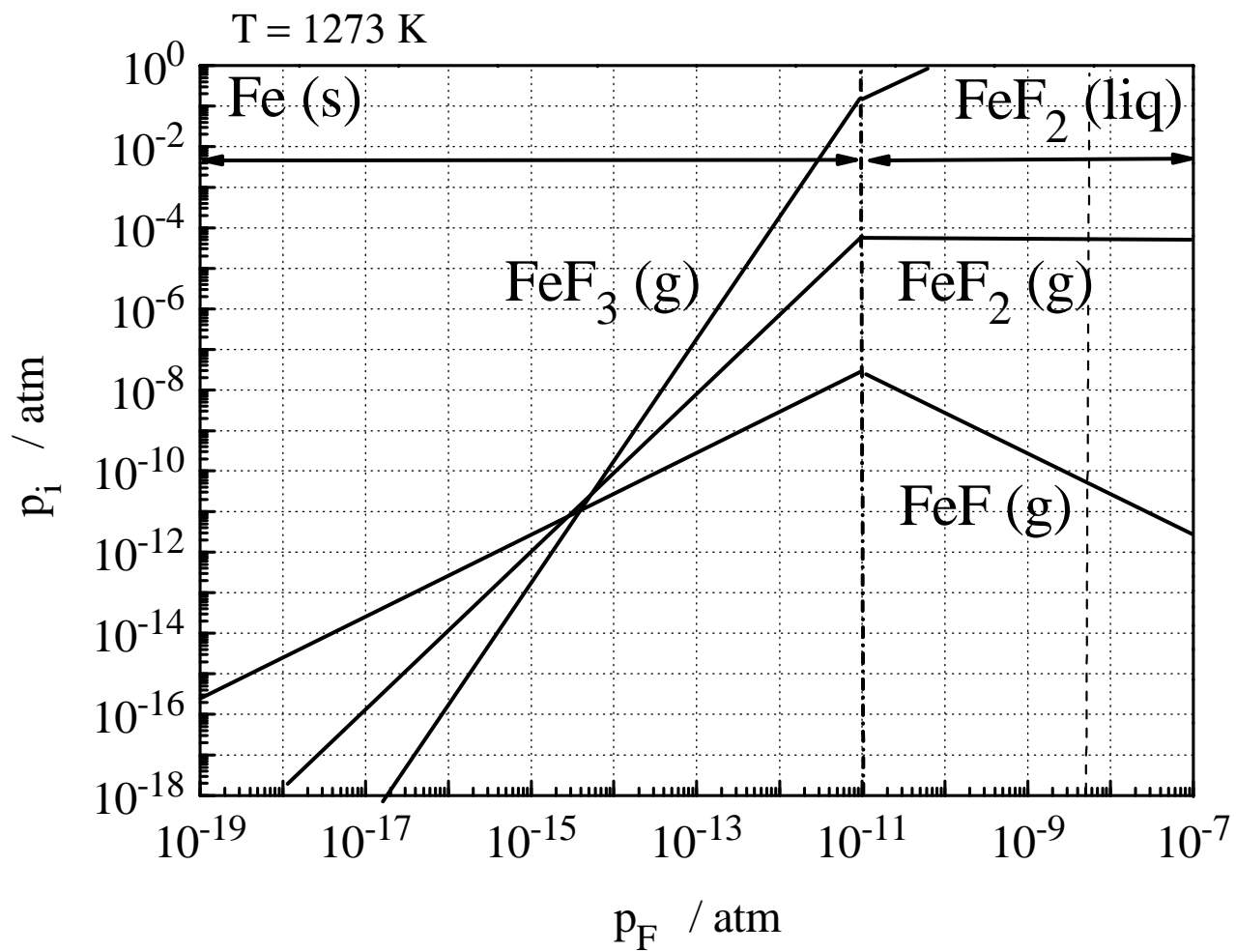
$$\log p_{\text{CrO}_{3(g)}} = \frac{3}{4} \log p_{\text{O}_2} + \log(\text{const})$$

# Ciśnienia lotnych tlenków

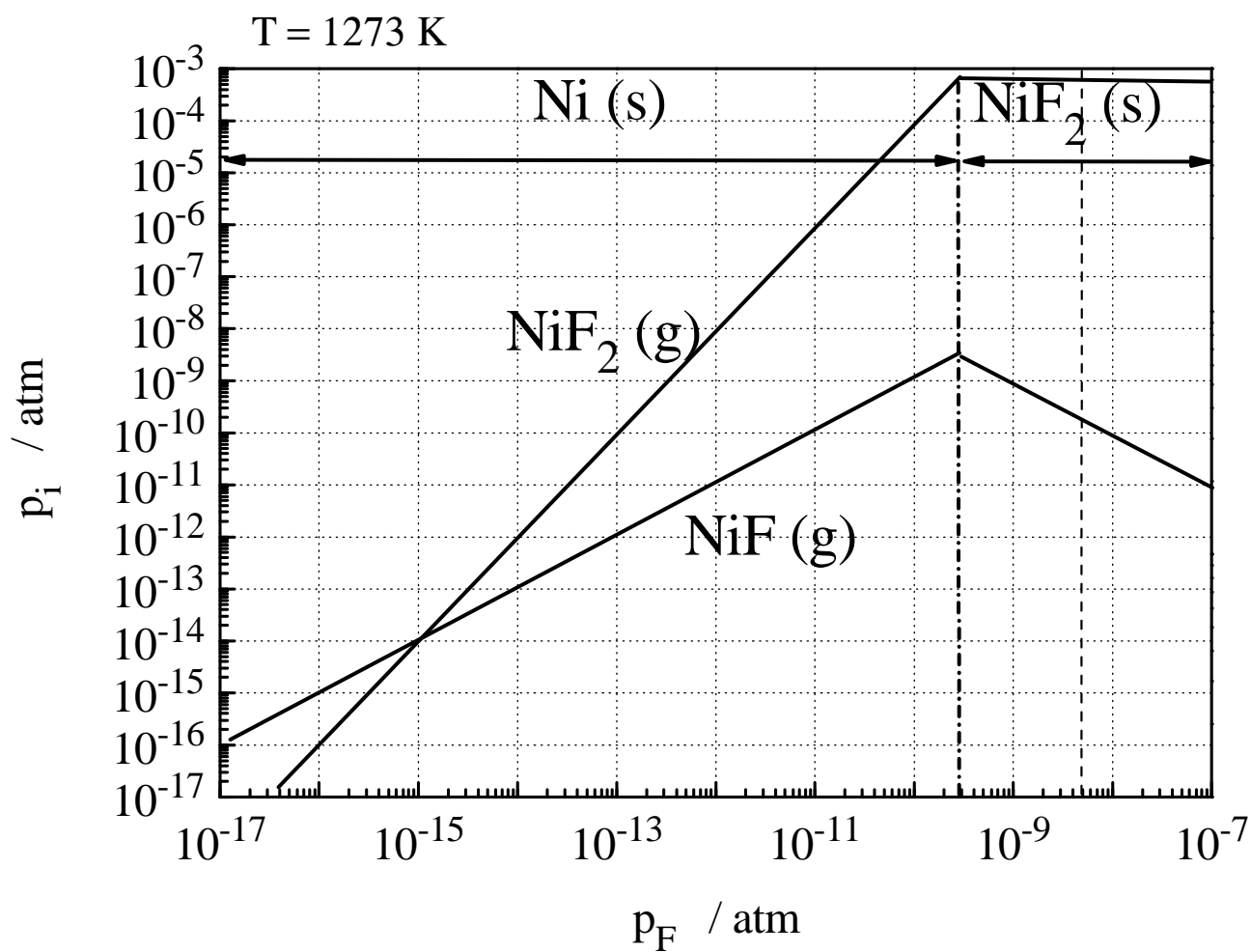




# Ciśnienia lotnych tlenków



# Ciśnienia lotnych tlenków





**KONIEC**