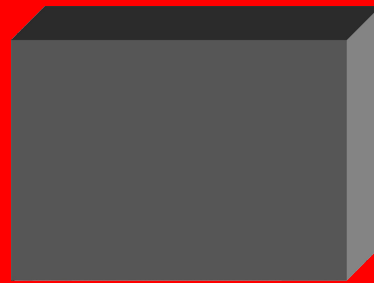


TERMODYNAMIKA PROCESÓW KOROZJI WYSOKOTEMPERATUROWEJ

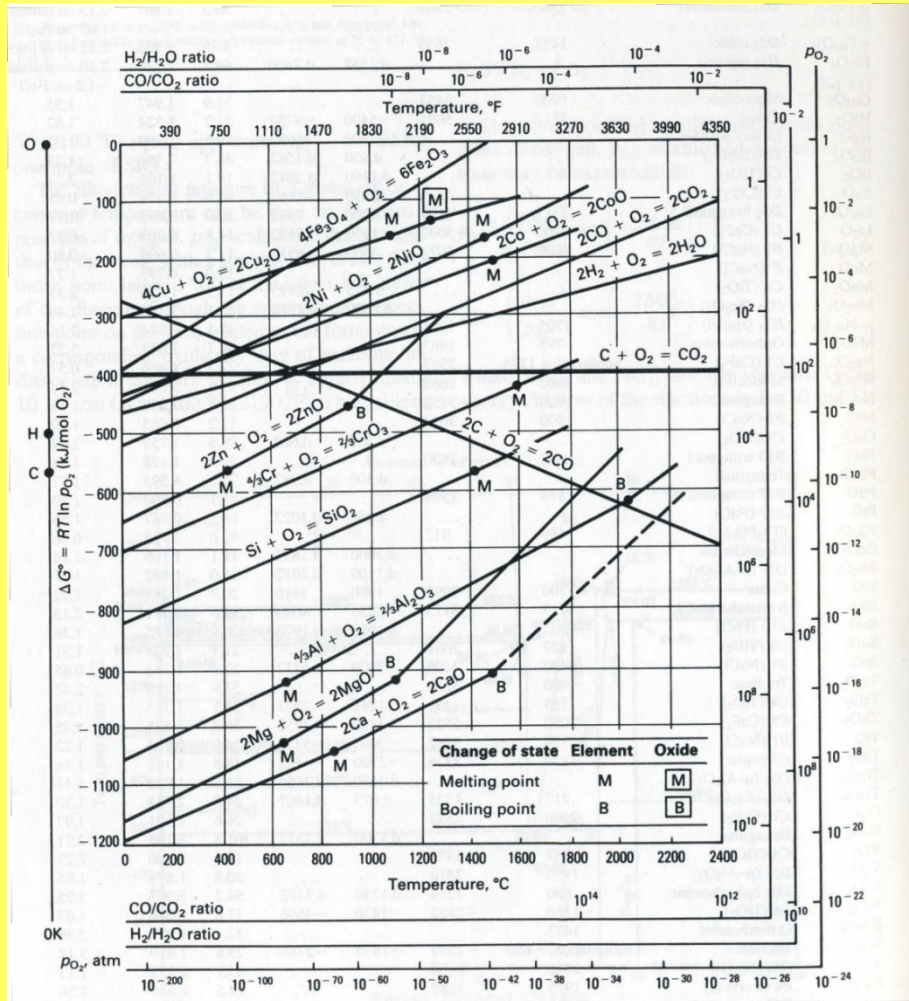
SCHEMAT PROCESU KOROZJI WYSOKOTEMPERATUROWEJ

$T = \text{const}$

$p = \text{const}$

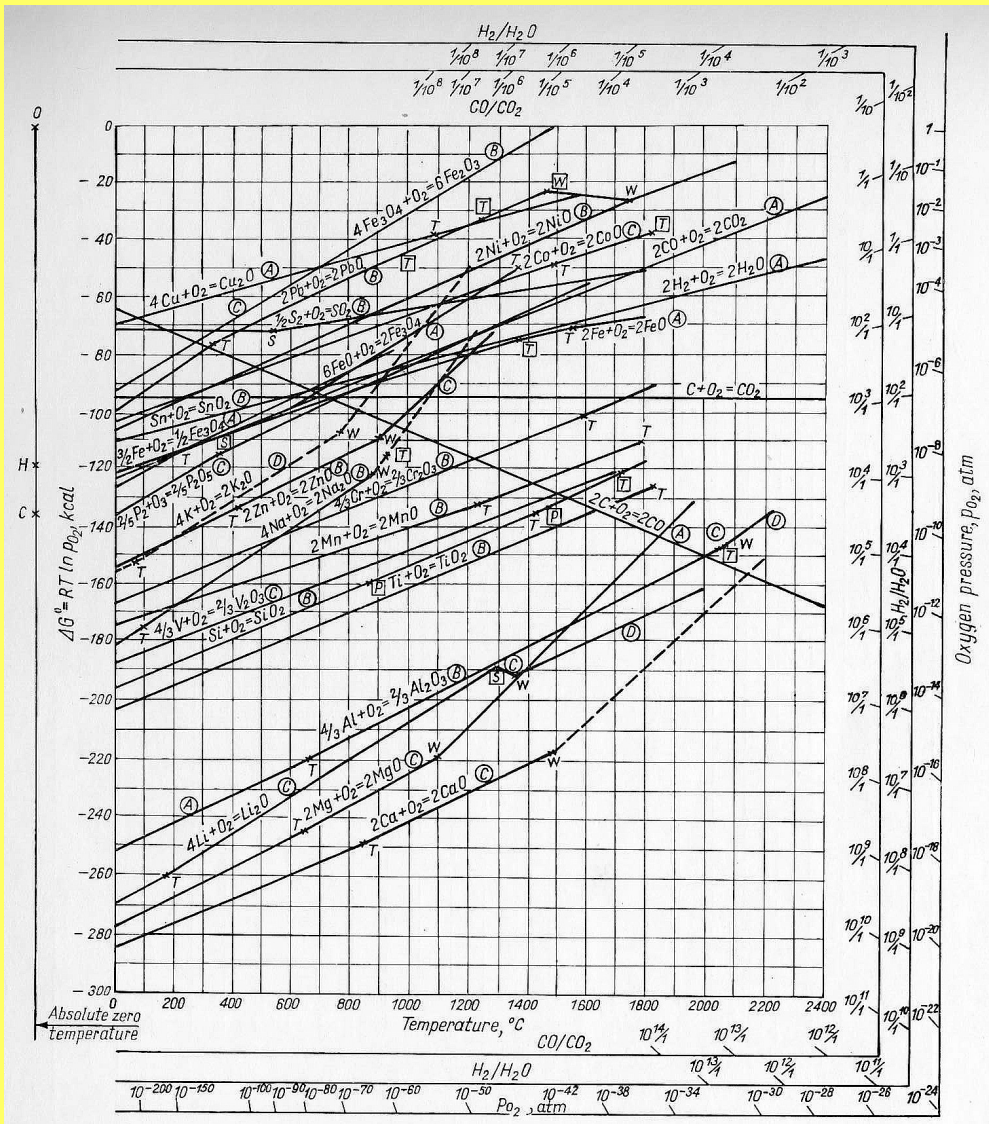


DIAGRAMY ELLINGHAM'A-RICHARDSON'A (RICHARDSON'A-JEFFES'A)

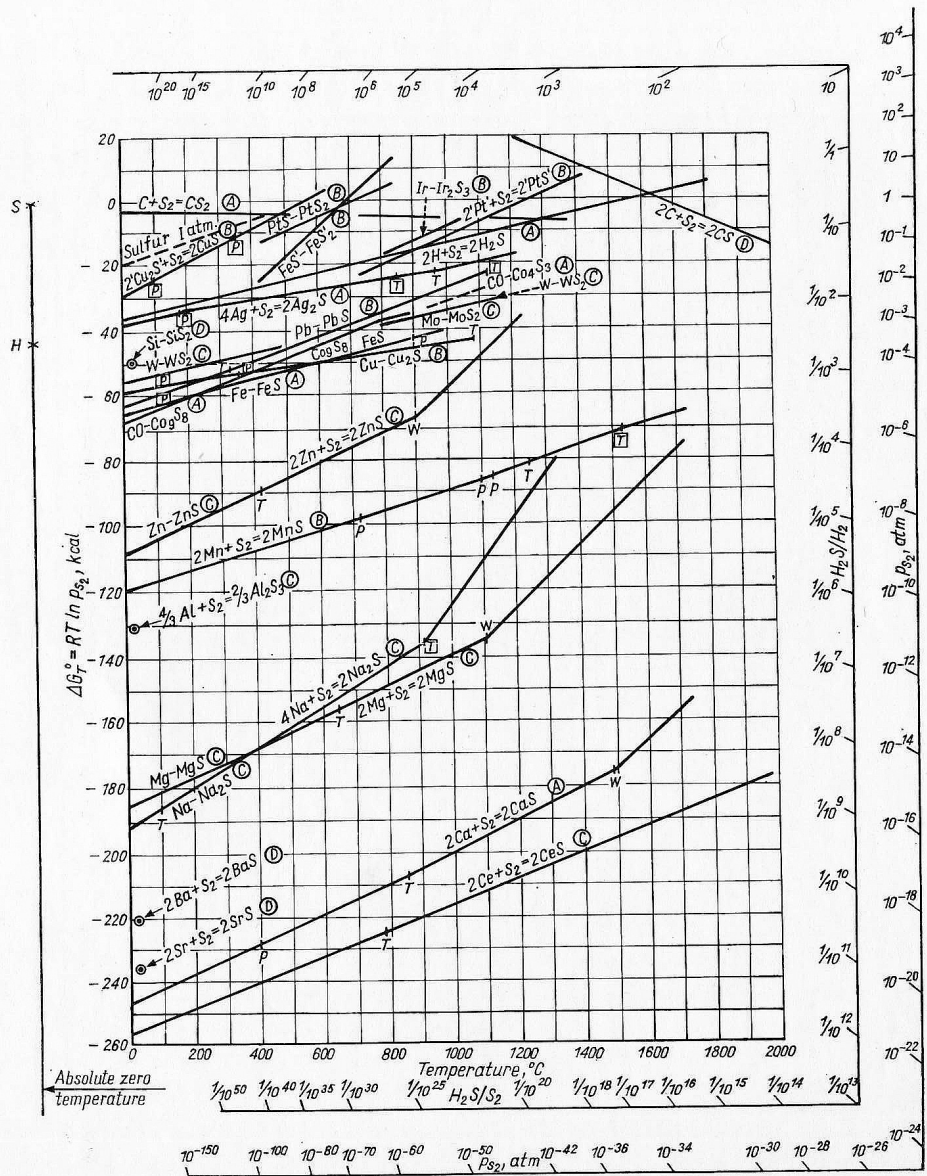


S. Mrowec, *An Introduction to the Theory of Metal Oxidation*, National Bureau of Standards and National Science Foundation, Washington D.C., 1982.

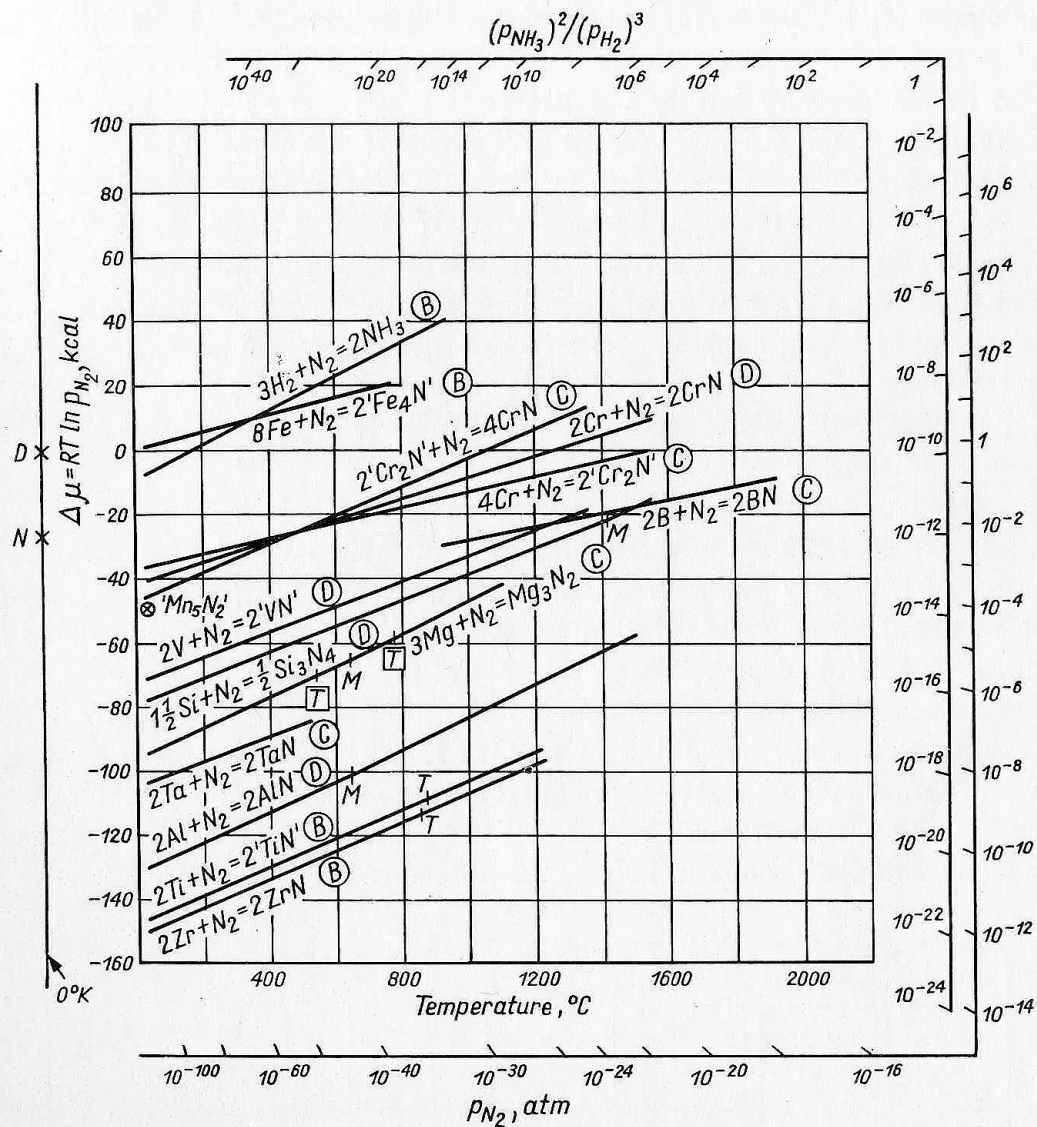
DIAGRAMY ELLINGHAM'A-RICHARDSON'A (RICHARDSON'A-JEFFES'A)



DIAGRAMY ELLINGHAM'A-RICHARDSON'A (RICHARDSON'A-JEFFES'A)

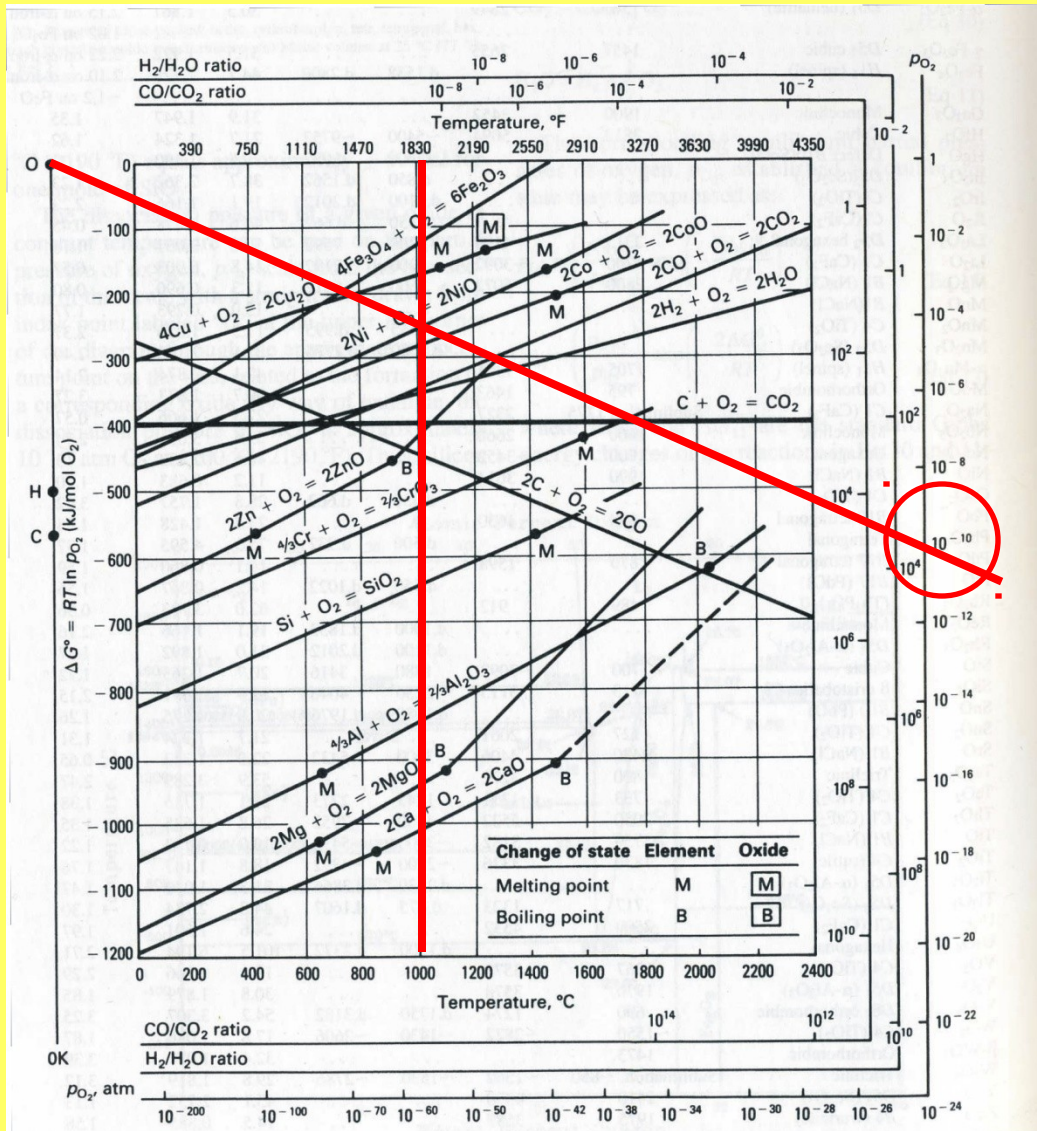


DIAGRAMY ELLINGHAM'A-RICHARDSON'A (RICHARDSON'A-JEFFES'A)



OKREŚLANIE CIŚNIEŃ DYSOCJACYJNYCH

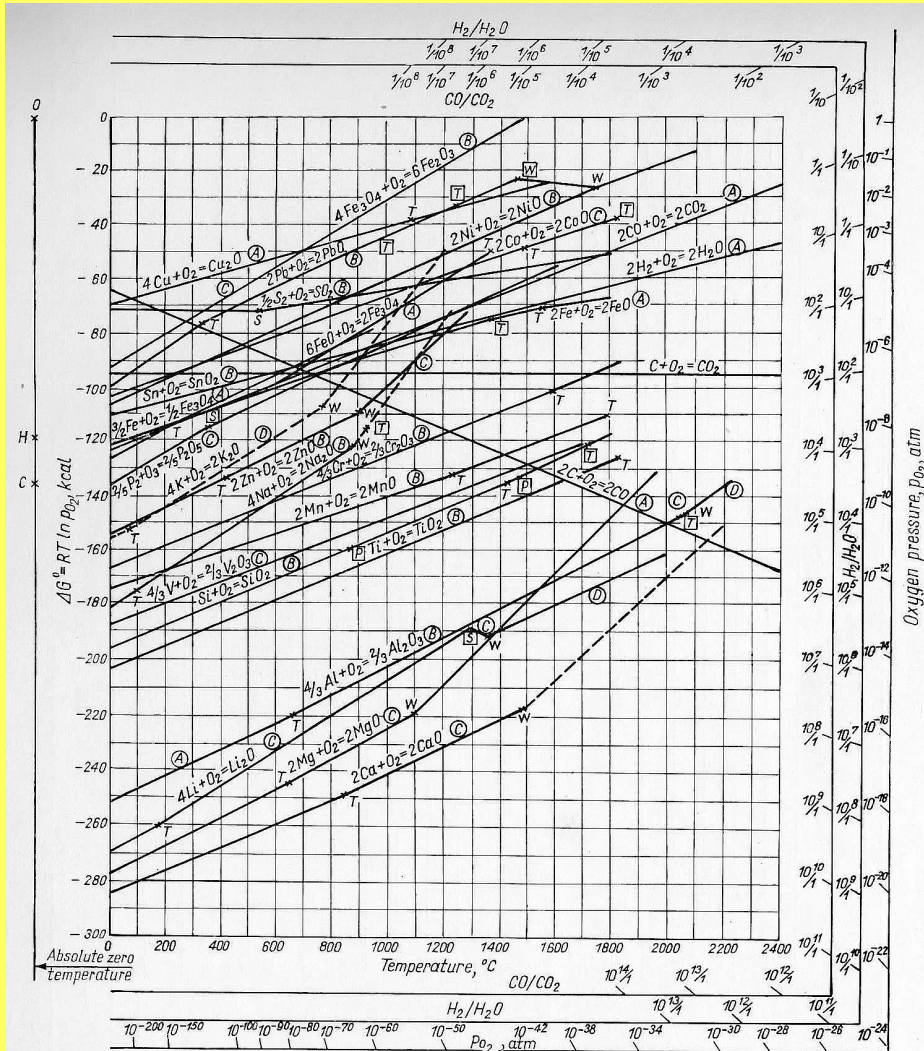
Przykład: określić ciśnienie dysocjacyjne NiO w $T = 1000\text{ }^{\circ}\text{C}$



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 $T = 1000\text{ }^\circ\text{C}$

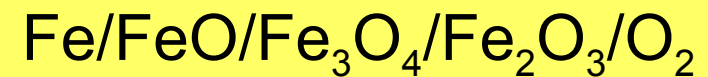


odp.:

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

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

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



OKREŚLANIE CIŚNIEŃ DYSOCJACYJNYCH



gdzie:

Me – metal

X₂ – 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_i – potencjał chemiczny danego składnika

$$\mu_i = \mu_i^0 + R T \ln a_i$$

gdzie:

R – stała gazowa

T – temperatura [K]

a_i – aktywność danego składnika w układzie

μ_i^0 – potencjał chemiczny danego składnika w warunkach standardowych, tj. przy jego aktywności równej jedności

W przypadku czystych substancji występujących w stanie stałym:

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

W przypadku substancji występujących w stanie gazowym:

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

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

W stanie równowagi termodynamicznej $\Delta G = 0$, a zatem:

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

TABLICE TERMODYNAMICZNE

J. Nedoma, M. Bućko, P. Schreiner, „Funkcje termodynamiczne”, AGH, Kraków, 1986

	T^0	$T \cdot 10^{-3}$	$T^2 \cdot 10^{-6}$	$T^3 \cdot 10^{-9}$	$T^{-1} \cdot 10^3$	$T^{-2} \cdot 10^5$	$\ln T$	$10^{-3} T \ln T$	T_1	T_2
--	-------	-------------------	---------------------	---------------------	---------------------	---------------------	---------	-------------------	-------	-------

Ag

	SILVER						sol		298.15	600
CP	5.6930	1.2230	-	-	-	-	-	-	6.058	6.427
H	-1.7517	5.6930	0.6115	-	-	-	-	-	-	1.884
S	-22.6011	1.2230	-	-	-	-	5.6930	-	10.200	14.550
G	-1.7517	28.2941	-0.6115	-	-	-	-	-5.6930	-3.041	-6.846
BT	-6.1845	0.1337	-	-	0.3829	-	1.2444	-	2.230	2.494

Ag

	SILVER						sol		600	1234
CP	4.7160	2.2940	-	-	-	1.2740	-	-	6.446	7.630
H	-1.1462	4.7160	1.1470	-	-0.1274	-	-	-	1.884	6.317
S	-16.8174	2.2940	-	-	-	-0.6370	4.7160	-	14.550	19.540
G	-1.1462	21.5334	-1.1470	-	-0.0637	-	-	-4.7160	-6.846	-17.796
BT	-4.7067	0.2507	-	-	0.2505	0.1392	1.0308	-	2.494	3.152

Ag

	SILVER						liq		1234	2436
CP	8.0000	-	-	-	-	-	-	-	8.000	8.000
H	-0.8550	8.0000	-	-	-	-	-	-	9.017	18.633
S	-35.2161	-	-	-	-	-	8.0000	-	21.728	27.169
G	-0.8550	43.2161	-	-	-	-	-	-8.0000	-17.795	-47.550
BT	-9.4461	-	-	-	0.1869	-	1.7486	-	3.152	4.266

$$\mu^0 [\text{kcal}] = G = a \cdot T^0 + b \cdot T \cdot 10^{-3} + c \cdot T^2 \cdot 10^{-6} + d \cdot T^3 \cdot 10^{-9} + e \cdot T^{-1} \cdot 10^3 + f \cdot T^{-2} \cdot 10^5 + g \cdot \ln T + h \cdot 10^{-3} \cdot T \cdot \ln T$$

TABLICE TERMODYNAMICZNE

I. Barin, O. Knacke, O. Kubaschewski, „Thermochemical properties of inorganic substances”, Springer-Verlag, Berlin-Heidelberg-New York, 1977

503

Chromium Cr

h°, μ° in J mol⁻¹ ; s°, c° in J K⁻¹ mol⁻¹ ; T in K ; $p = P/\text{bar}$

$$c^{\circ} = a + b \cdot 10^{-3} T + c \cdot 10^6 T^{-2} + d \cdot 10^{-6} T^2$$

$$\lg(p, K) = e \cdot 10^3 T^{-1} + f \cdot \lg T + g$$

Coefficients of c° and integration constants of enthalpy and entropy

Phase	a	b	c	d	H ⁺	S ⁺	T	Ref.
S	24.514	2.050	-0.180	5.950	-8.056	-117.919	298	103,111,e
L	39.330				4.784	-203.957	2130	103,111
G	20.983	-1.992	0.038	1.828	391.422	55.484	2954	103,111,e

Coefficients of $\lg(p, K)$

Phase	e	f	g	Ref.
S	-21.920	-2.79	17.223	103,111,e
L	-19.460	-1.36	11.308	103,111,e

$T_{\lambda} = 311.5 \text{ K [111]}$;

Vapor: $\text{Cr}^{\text{S,L}} = \text{Cr}^{\text{G}}$;
 $T_b = 2952 \text{ K}$; $\Delta S_b = 27.5 \text{ cal/K mol}$; [103,111]

Phase	T	c ^o	h ^o	s ^o	μ ^o	β ^o	p, K	Ref.
S	298	23.63	0	23.640	-7048	1.235		103,111,190
	300	23.67	43	23.786	-7092	1.235		
	400	25.16	2490	30.814	-9835	1.284		
	500	26.31	5065	36.555	-13212	1.380		
	600	27.39	7749	41.446	-17118	1.490		
	700	28.50	10543	45.751	-21482	1.603		
	800	29.68	13451	49.632	-26254	1.714		
	900	30.96	16482	53.201	-31398	1.822		
	1000	32.33	19646	56.533	-36886	1.927		
	1100	33.82	22953	59.683	-42698	2.028		
	1200	35.42	26413	62.694	-48818	2.125		
	1300	37.13	30040	65.595	-55233	2.219	0.472 E-8	
	1400	38.95	33843	68.413	-61934	2.311	0.614 E-7	
	1500	40.90	37834	71.166	-68914	2.400	0.560 E-6	
	1600	42.96	42026	73.870	-76166	2.487	0.383 E-5	
	1700	45.13	46429	76.539	-83687	2.571	0.207 E-4	
	1800	47.43	51056	79.183	-91473	2.654	0.918 E-4	
1900	49.84	55918	81.812	-99523	2.736	0.345 E-3		
2000	52.37	61028	84.432	-107835	2.816	0.113 E-2		
2100	55.02	66396	87.050	-116409	2.895	0.328 E-2		
2130	55.83	68059	87.837	-119032	2.919	0.442 E-2		
L			20497	9.623				103,111
	2130	39.33	88556	97.460	-119032	2.919	0.442 E-2	
	2200	39.33	91309	98.732	-125899	2.989	0.826 E-2	
	2300	39.33	95242	100.480	-135861	3.085	0.188 E-1	
	2400	39.33	99175	102.154	-145993	3.177	0.400 E-1	
	2500	39.33	103108	103.759	-156289	3.265	0.799 E-1	

$$\mu^{\circ} = 10^3 \cdot \left[H^{\circ} + S^{\circ} \cdot y - a \cdot y \cdot (\ln(T/K) - 1) - \frac{b}{2} \cdot y^2 - \frac{c}{2} \cdot y^{-1} - \frac{d}{6} \cdot y^3 \right]$$

$$y = 10^{-3} \cdot T / K$$

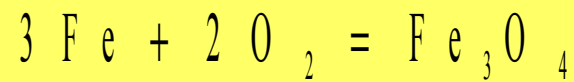
KOLEJNOŚĆ TLENKÓW W ZGORZELINIE WIELOFAZOWEJ

Przykład: określić kolejność występowania tlenków w zgorzelinie powstającej na żelazie, utlenianym w powietrzu w $T = 1000 \text{ }^\circ\text{C}$

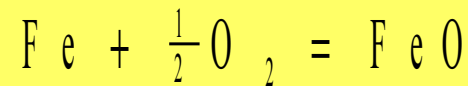


PRZYKŁADY BŁĘDNEGO STOSOWANIA ROZWAŻAŃ TERMODYNAMICZNYCH

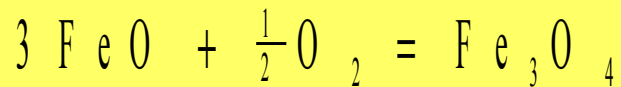
Określenie kolejności występowania warstw tlenkowych w zgorzelinie wielofazowej:



$$p(\text{Fe}_3\text{O}_4) = 3.1 \cdot 10^{-15} \text{ atm}$$



$$p(\text{FeO}) = 2.7 \cdot 10^{-16} \text{ atm}$$



$$p(\text{Fe}_3\text{O}_4) = 4.6 \cdot 10^{-12} \text{ atm}$$

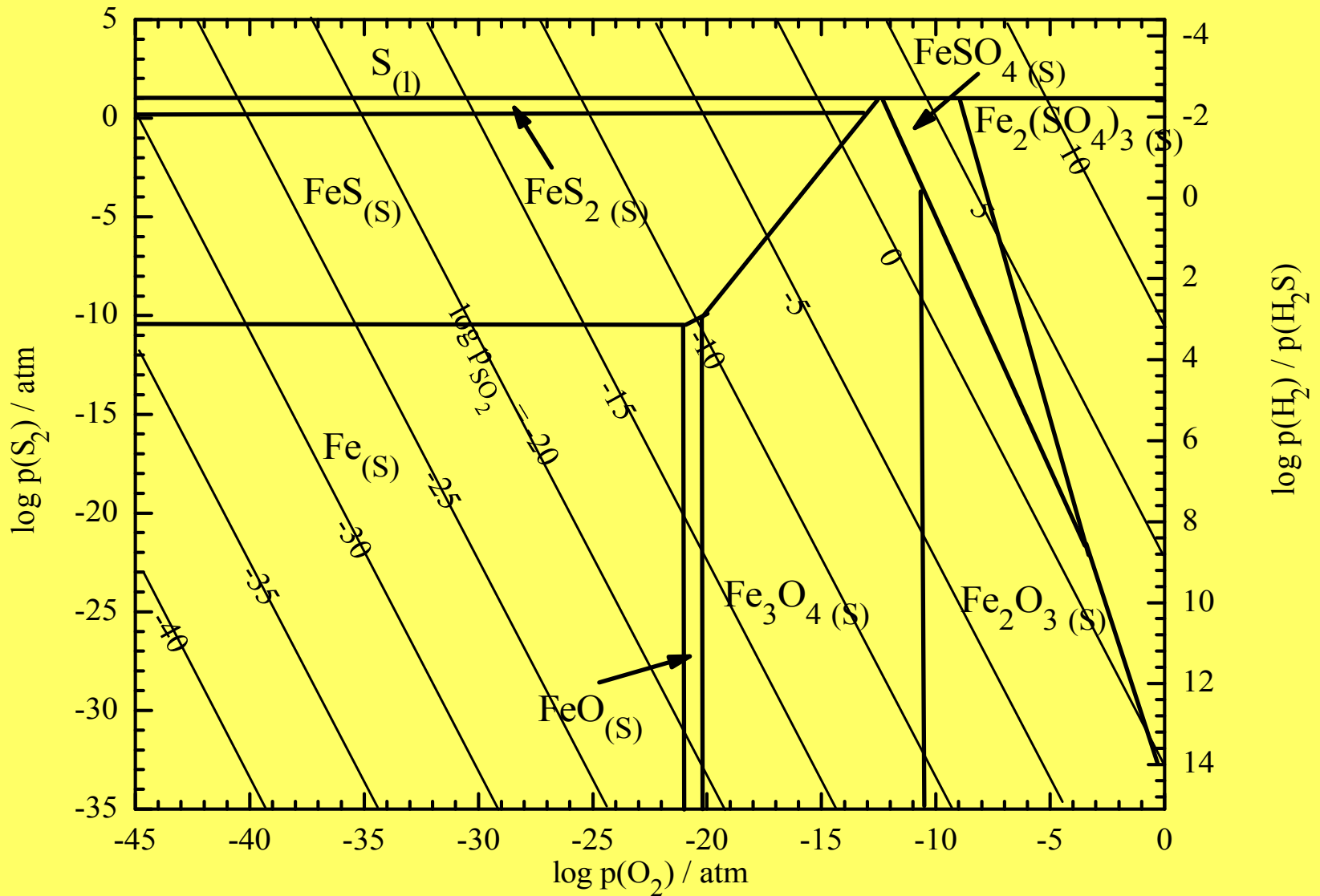
Występowanie określonych produktów reakcji w układach wieloskładnikowych:



$$\Delta G < 0$$

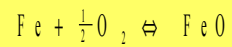
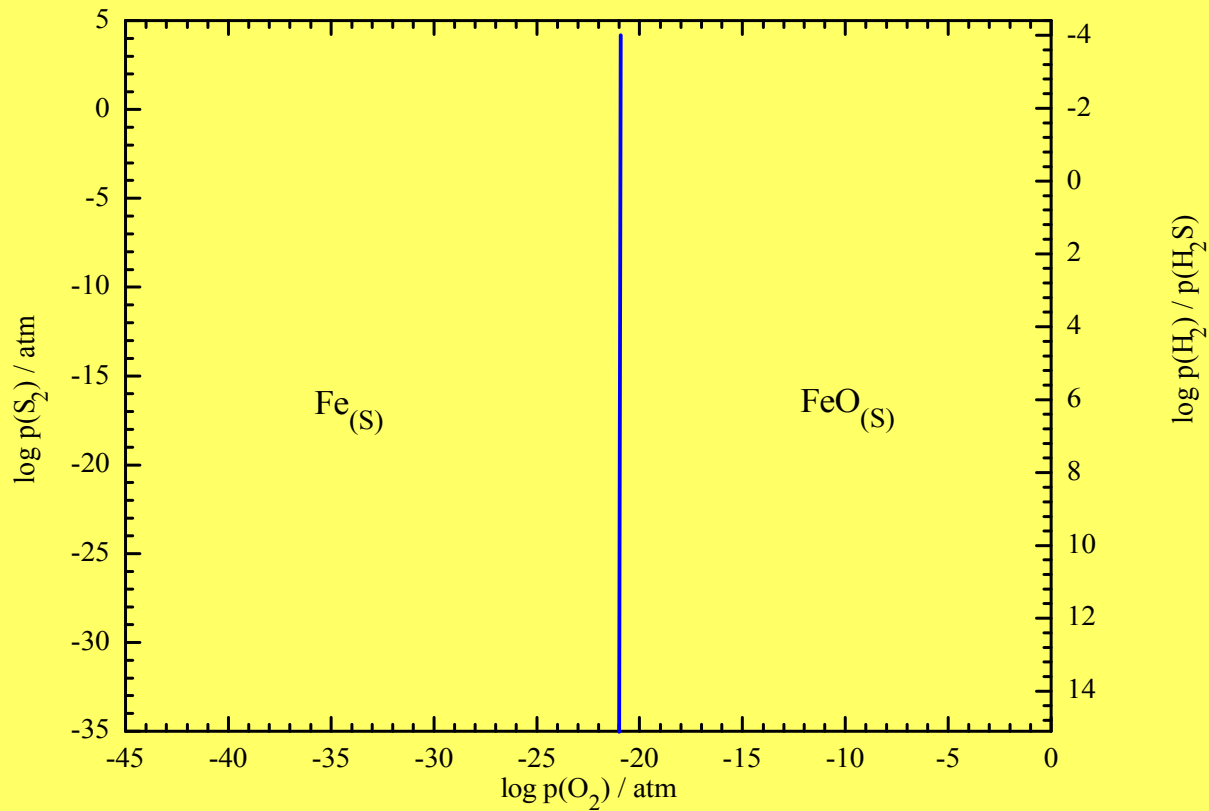
$$\Delta G > 0$$

DIAGRAMY KELLOGG'A

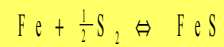
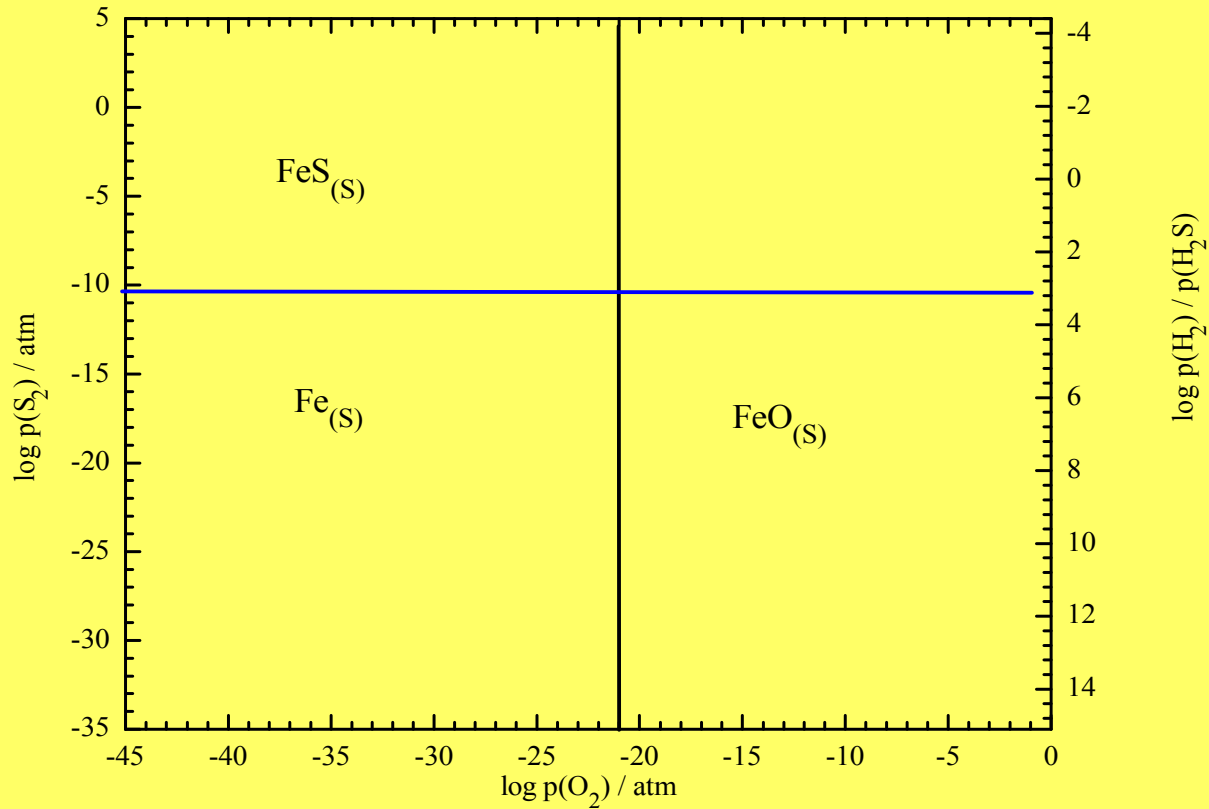


Z. Grzesik, "Thermodynamics of gaseous corrosion" in ASM Handbook, vol. 13a, p.90-96, ASM International, Materials Park, Ohio, USA, 2003.

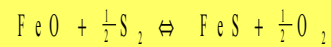
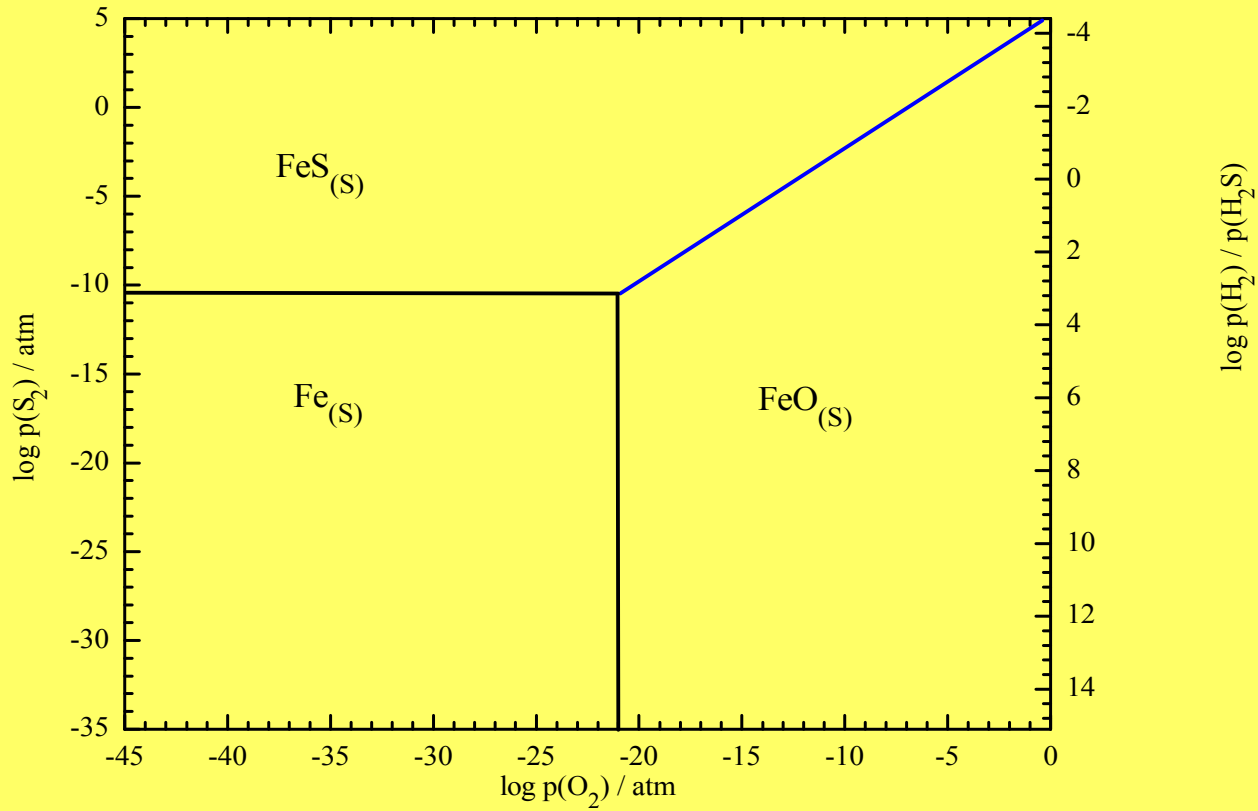
DIAGRAMY KELLOGG'A



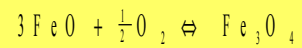
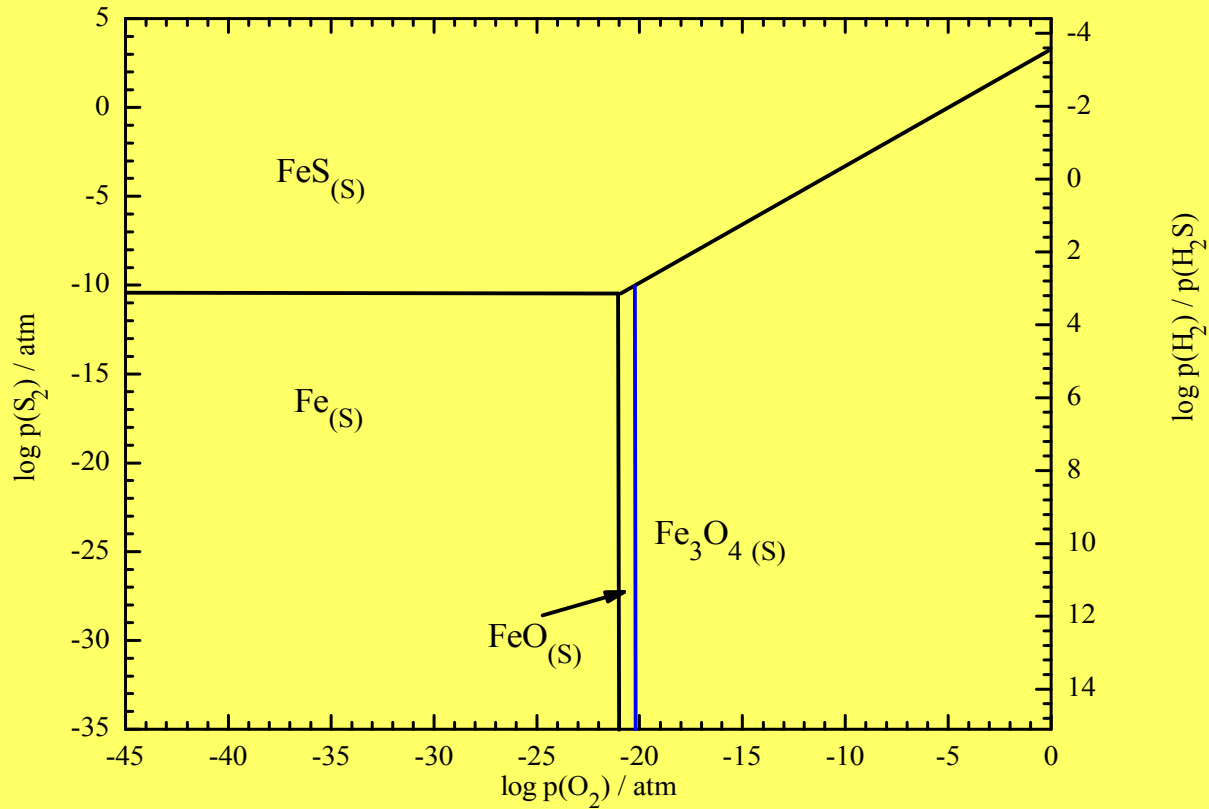
DIAGRAMY KELLOGG' A



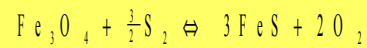
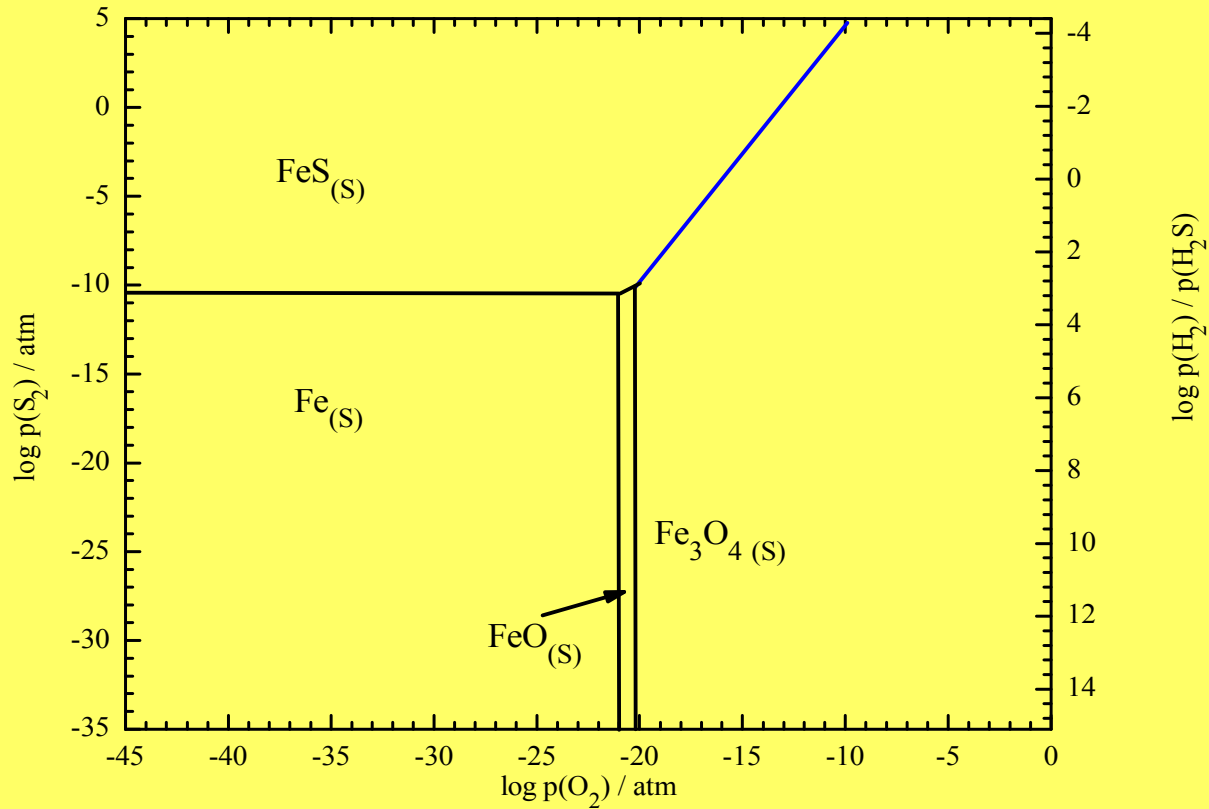
DIAGRAMY KELLOGG'A



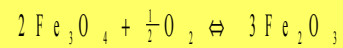
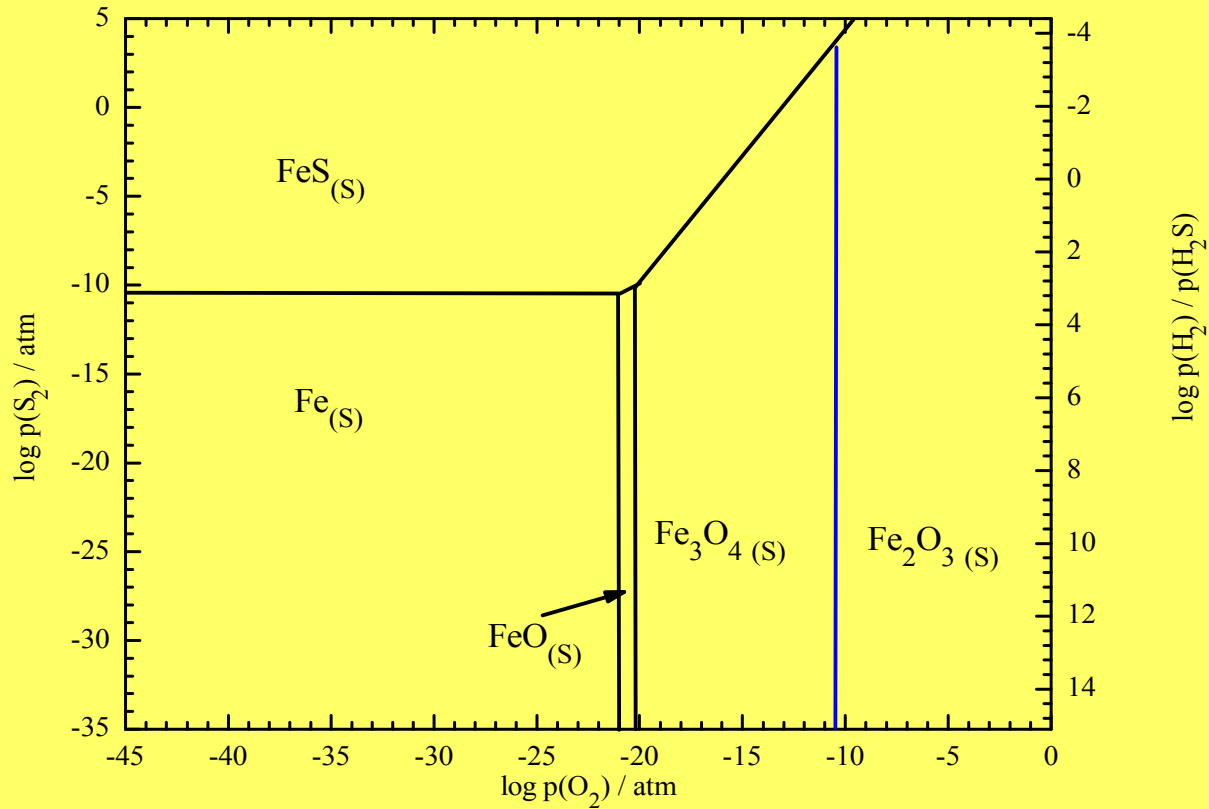
DIAGRAMY KELLOGG' A



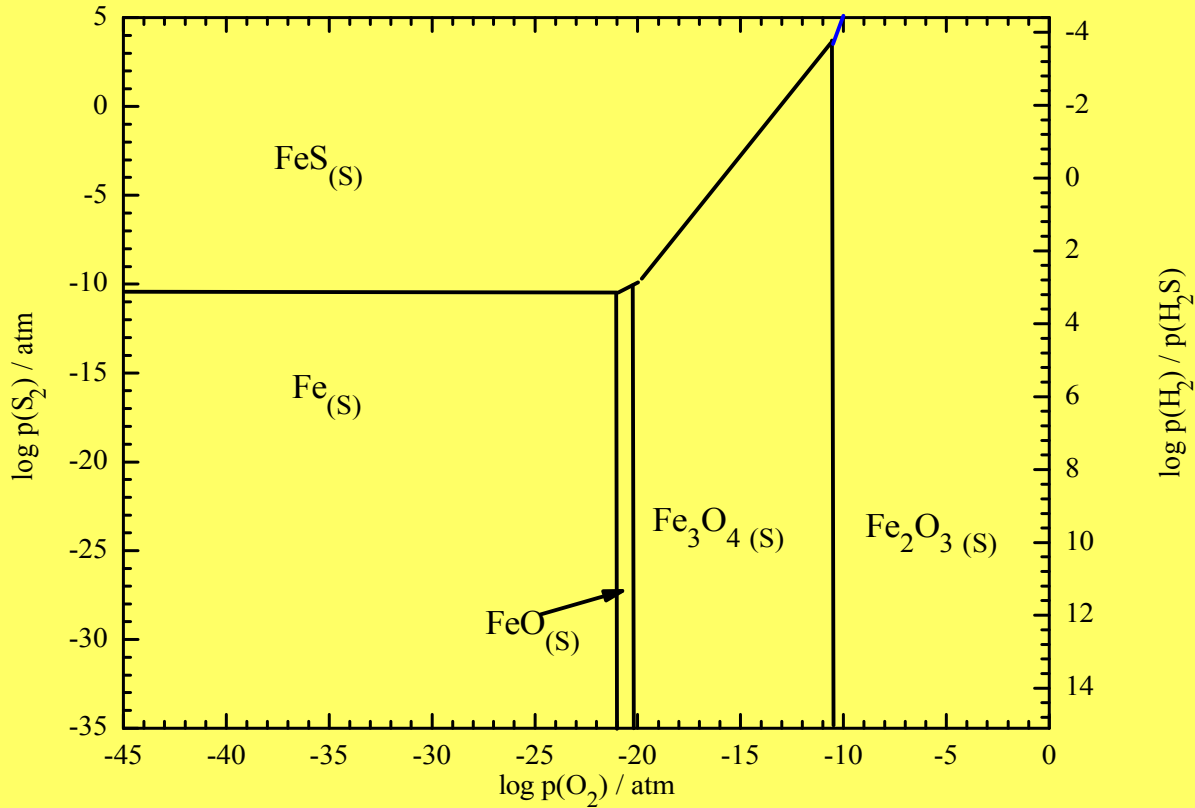
DIAGRAMY KELLOGG' A



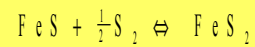
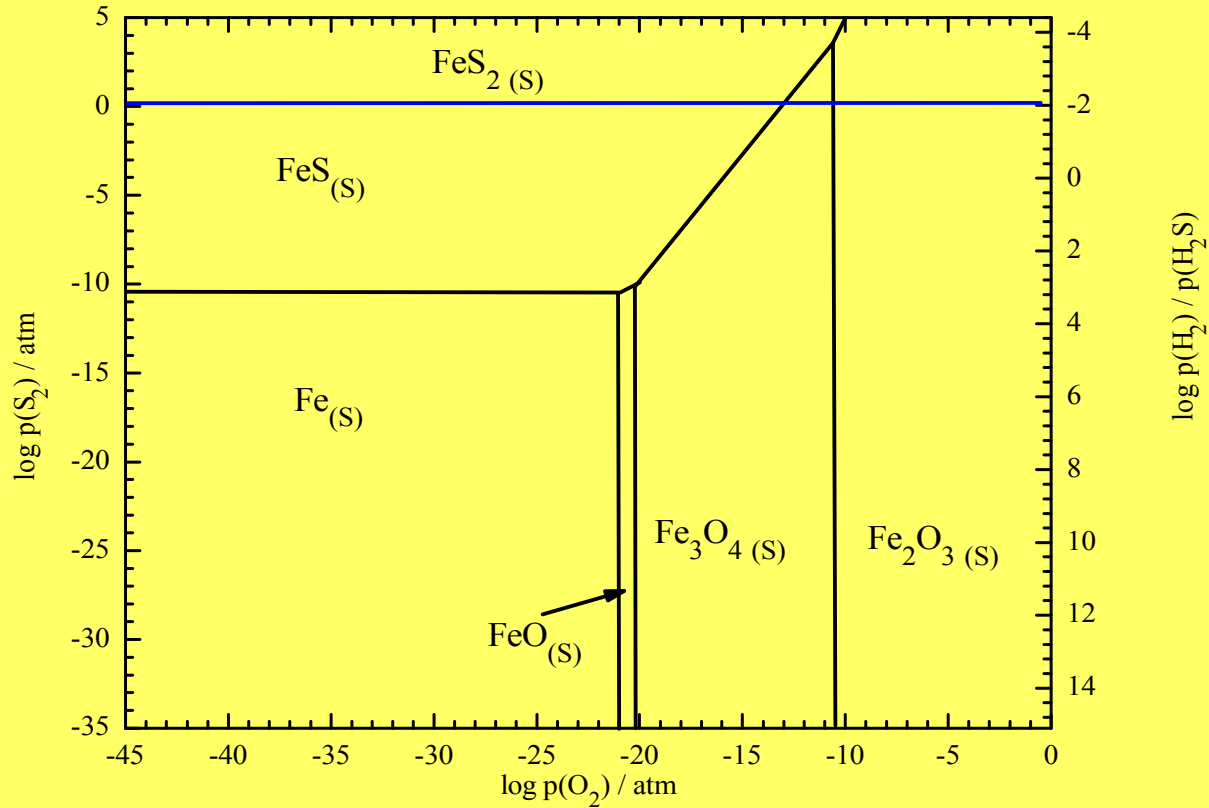
DIAGRAMY KELLOGG'A



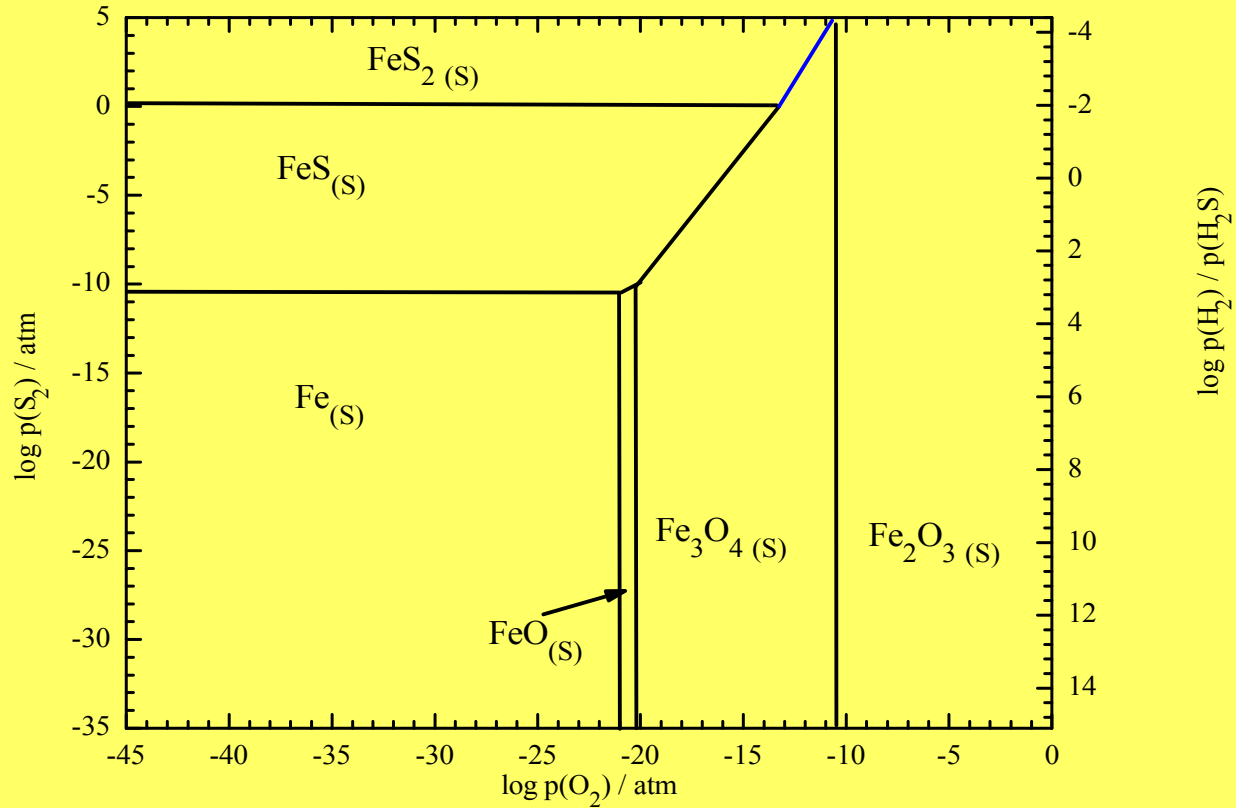
DIAGRAMY KELLOGG'A



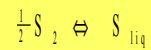
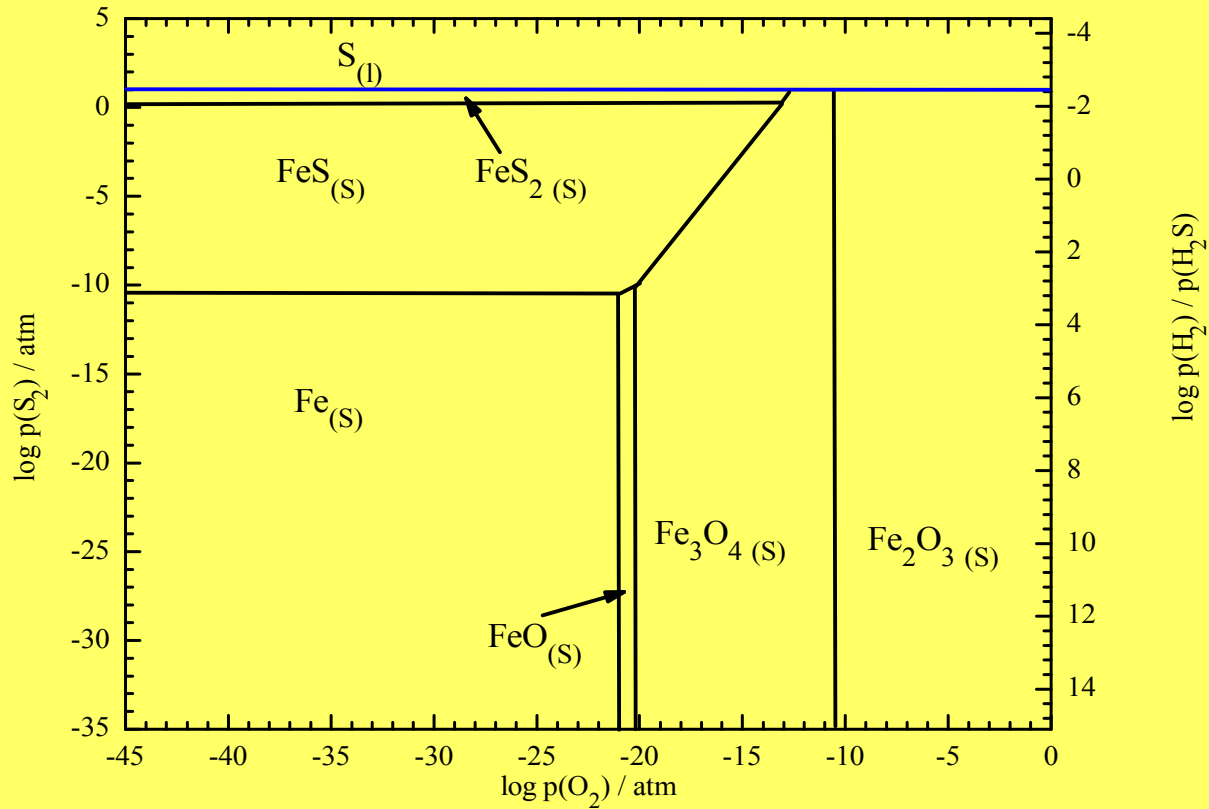
DIAGRAMY KELLOGG' A



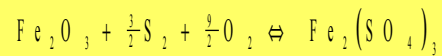
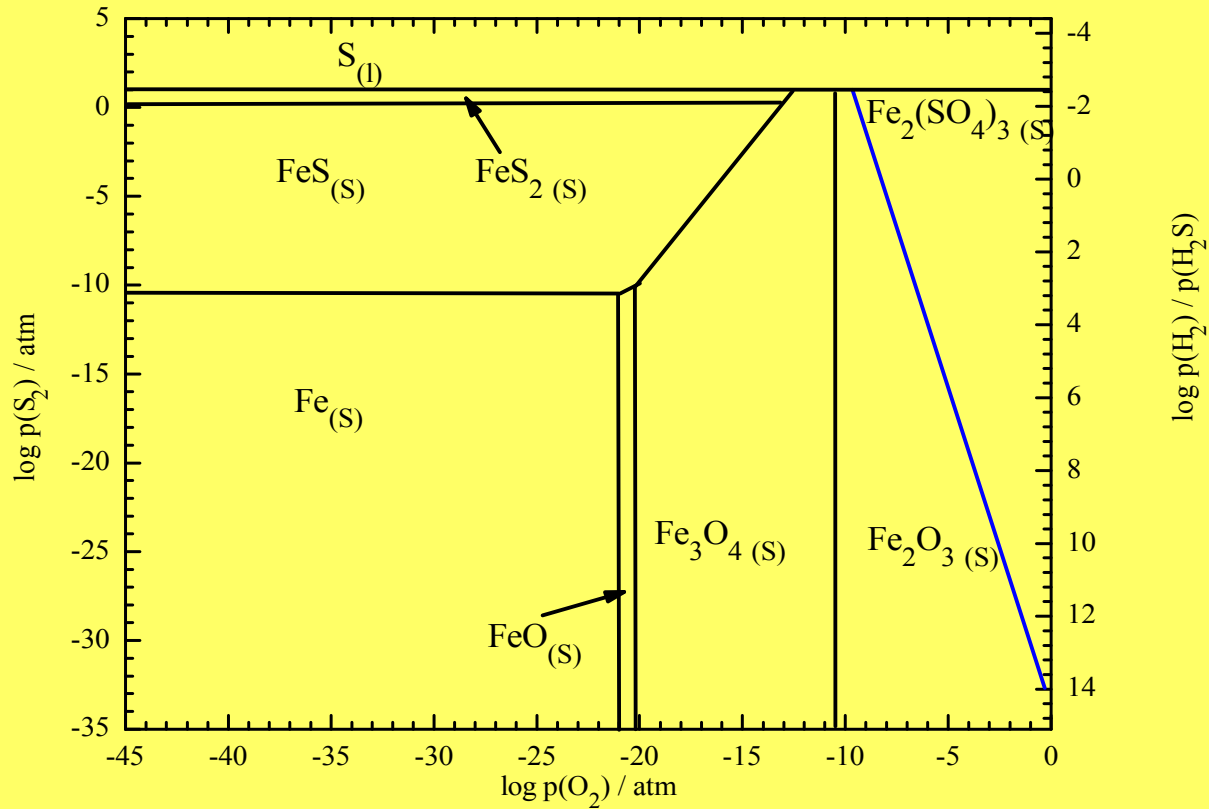
DIAGRAMY KELLOGG'A



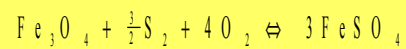
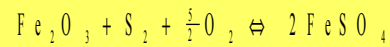
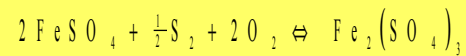
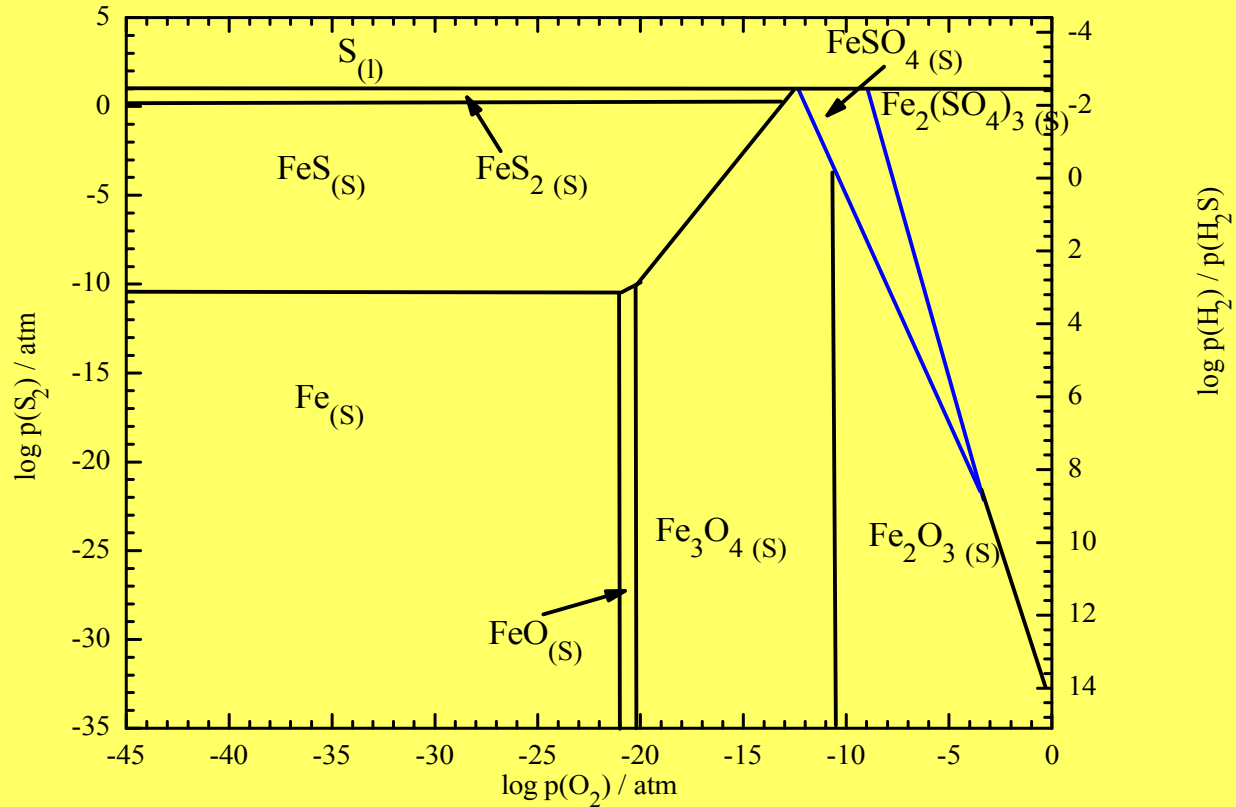
DIAGRAMY KELLOGG' A



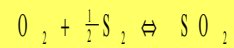
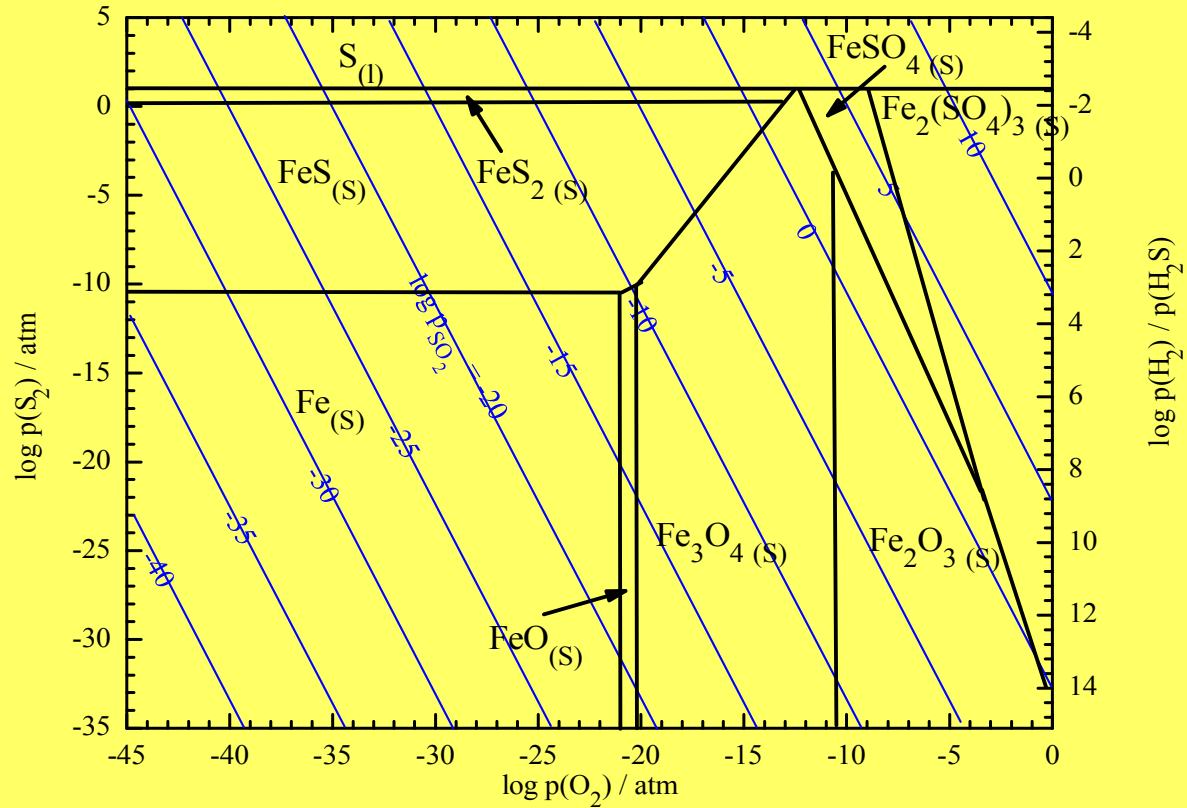
DIAGRAMY KELLOGG' A



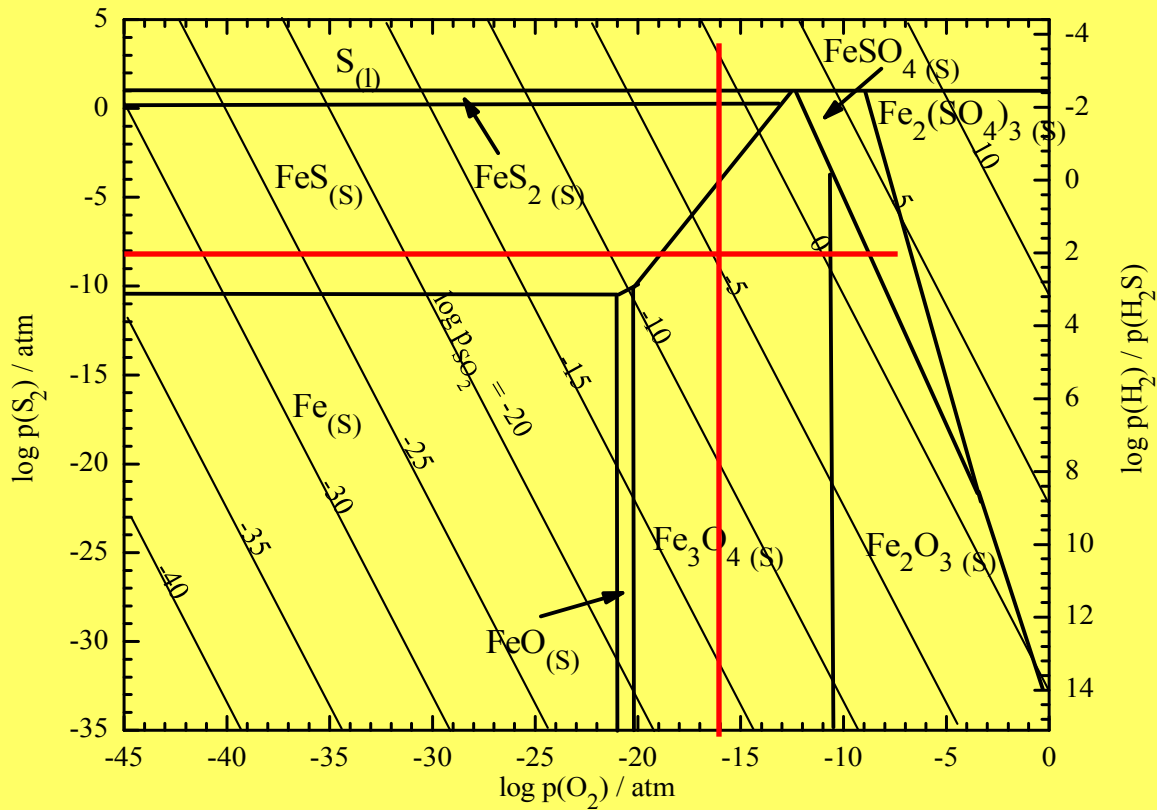
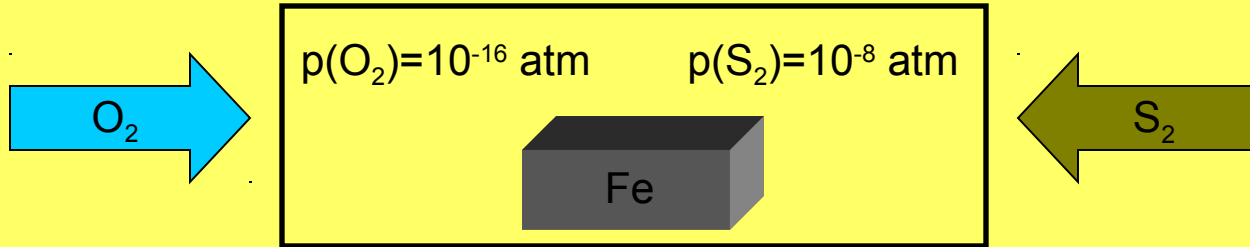
DIAGRAMY KELLOGG' A



DIAGRAMY KELLOGG'A

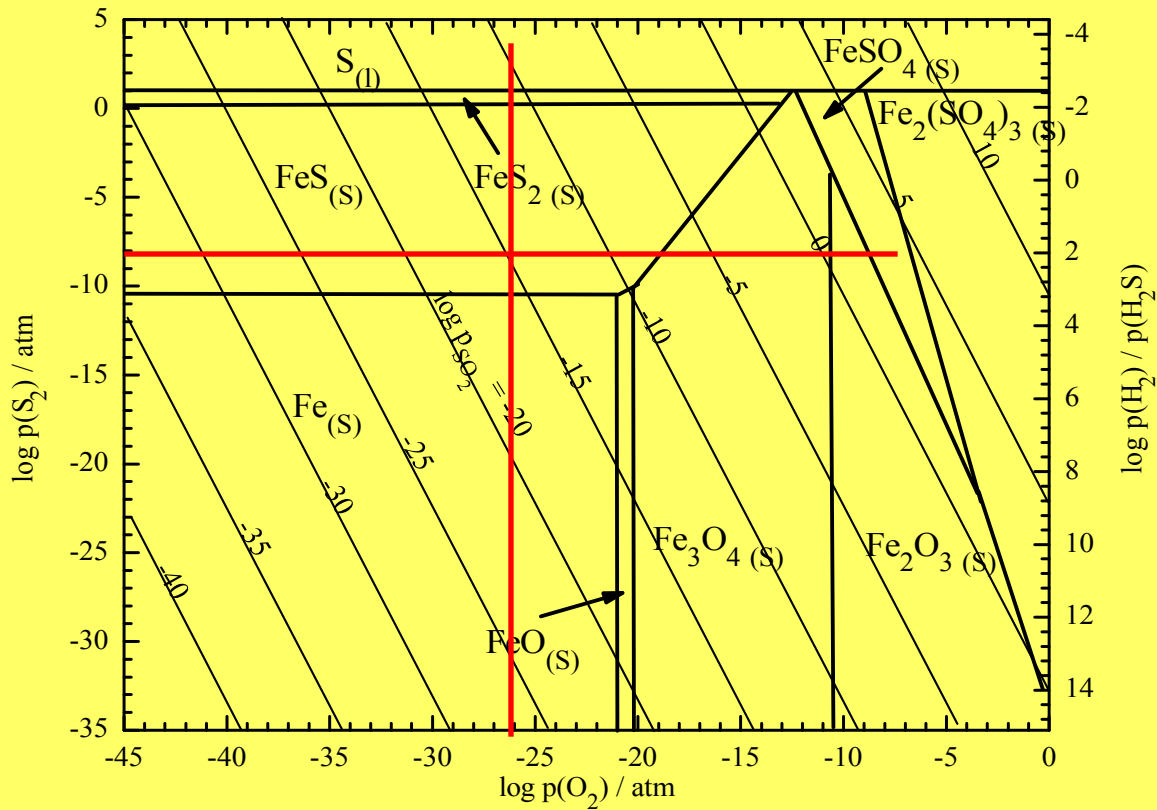
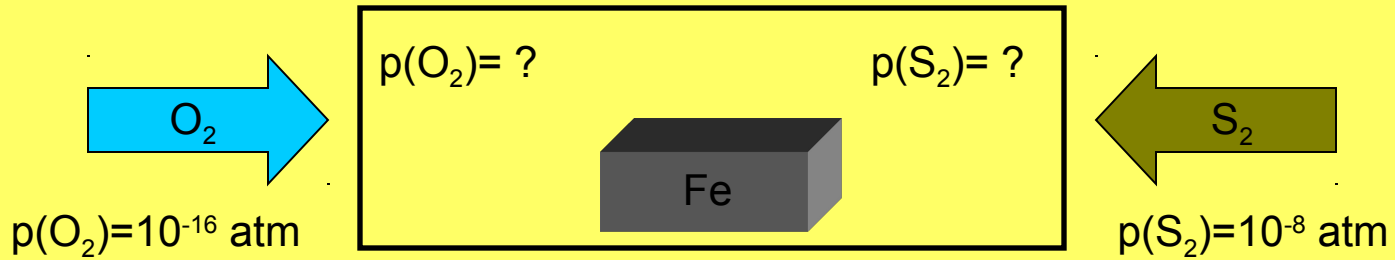


DIAGRAMY KELLOGG'A



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

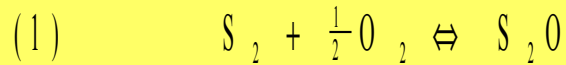
DIAGRAMY KELLOGG'A



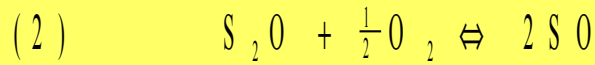
odp.: Fe → FeS

CIŚNIENIA CZĄSTKOWE GAZÓW W MIESZANINACH

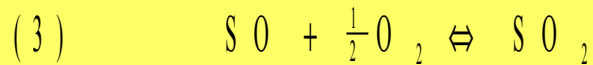
Układ tlen - siarka



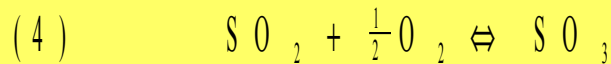
$$p_{O_2} = \left(\frac{p_{S_2O}}{p_{S_2}} \right)^2 \cdot \exp \left(\frac{2 \Delta G_1^0}{R T} \right)$$



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



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



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

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

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

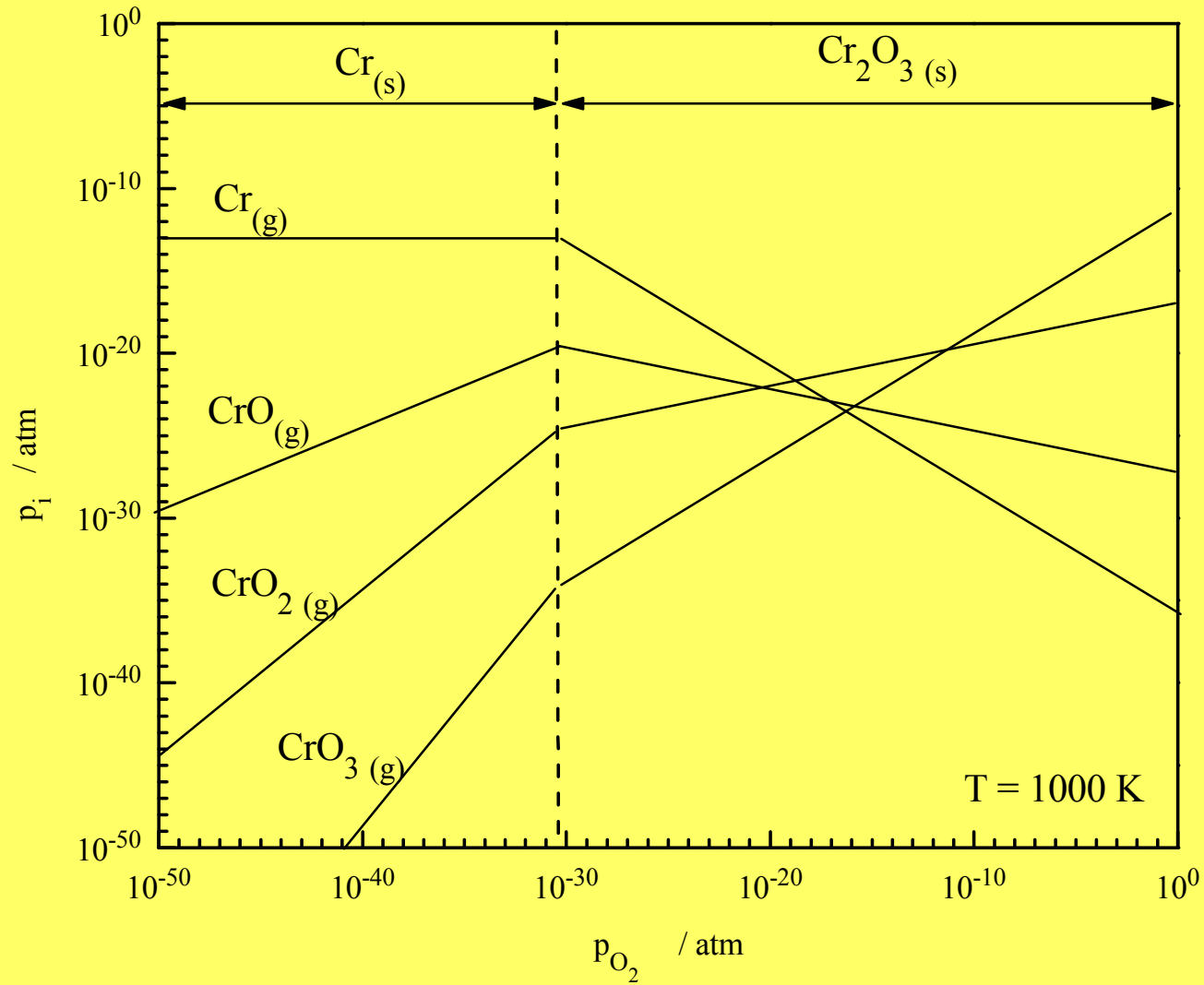
gdzie N_S i N_{O_2} oznaczają całkowite ilości moli S i O_2 obecnych w systemie, natomiast

n_{S_2} , n_{S_2O} , n_{SO} , n_{SO_2} , n_{SO_3} , n_{O_2} – ilość moli poszczególnych gazów w stanie równowagi termodynamicznej.

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

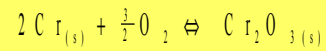
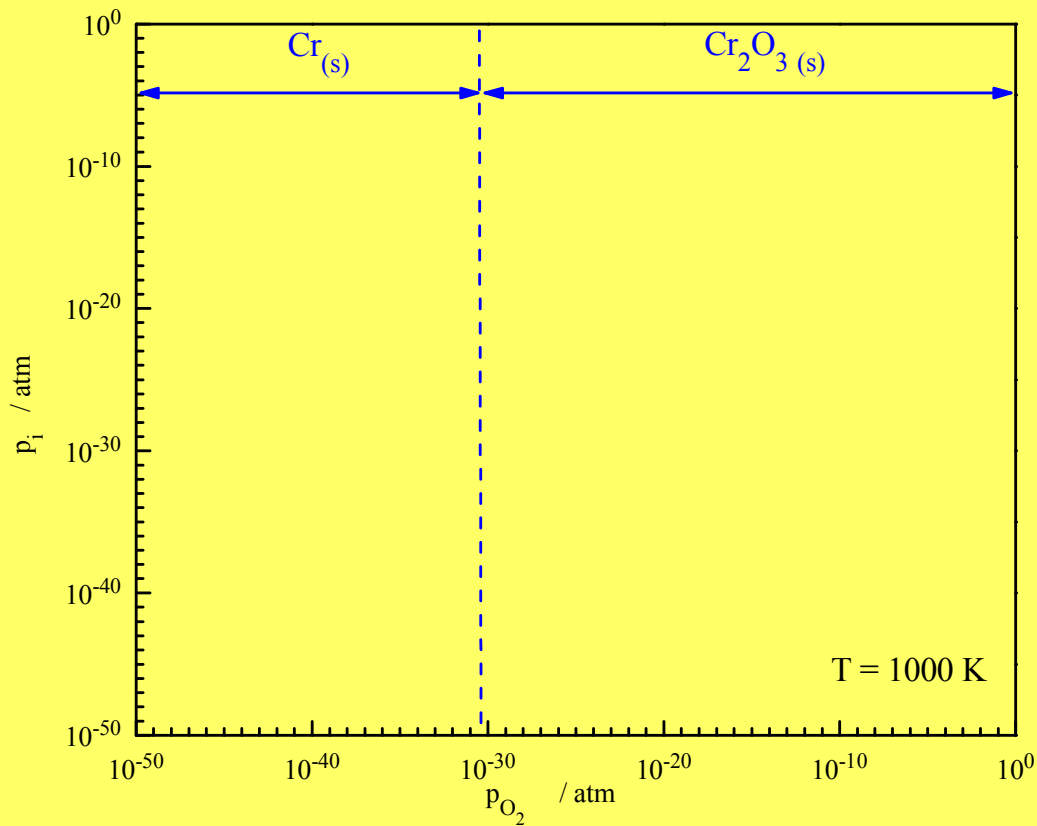
gdzie n_i jest ilością moli składnika i, m – liczbą wszystkich składników w układzie, natomiast p_{tot} oznacza całkowite ciśnienie mieszaniny gazowej.

CIŚNIENIA LOTNYCH TLENKÓW



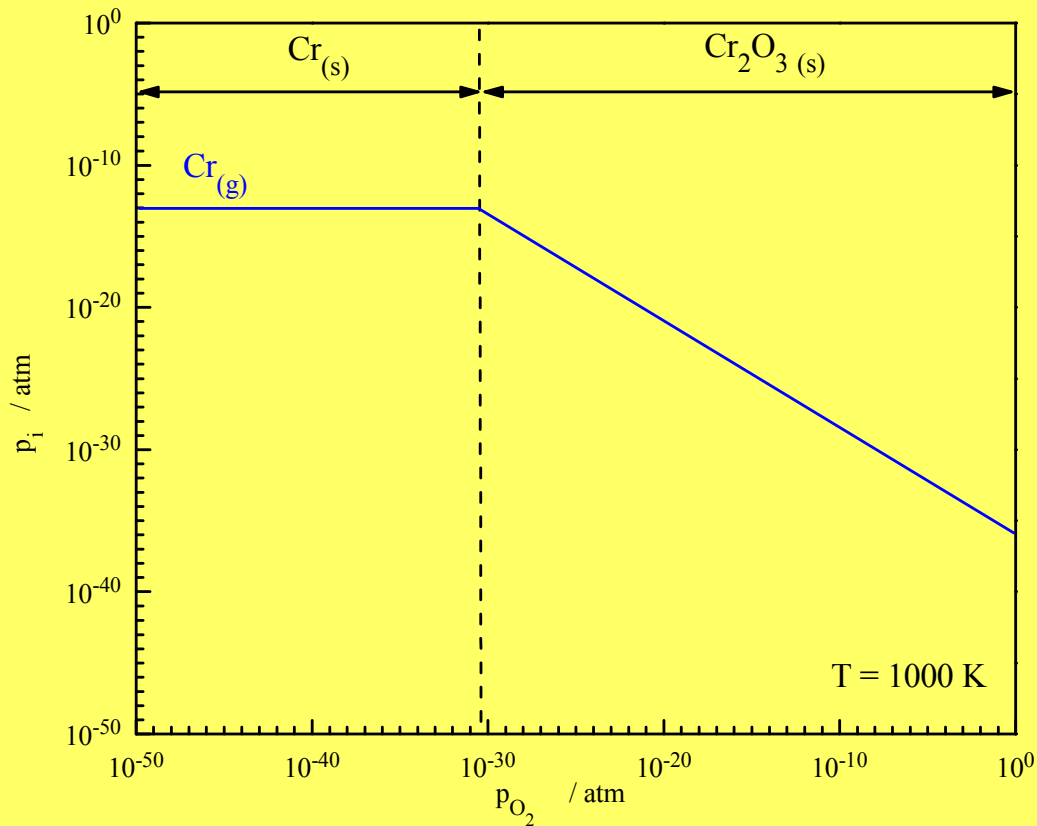
Z. Grzesik, "Thermodynamics of gaseous corrosion" in ASM Handbook, vol. 13a, p.90-96, ASM International, Materials Park, Ohio, USA, 2003.

CIŚNIENIA LOTNYCH TLENKÓW

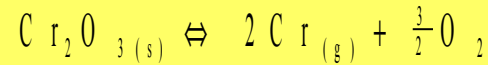


$$p_{\text{O}_2} = \exp\left(\frac{2 \Delta G^0}{3RT}\right)$$

CIŚNIENIA LOTNYCH TLENKÓW

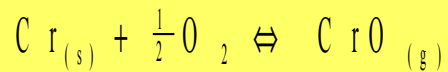
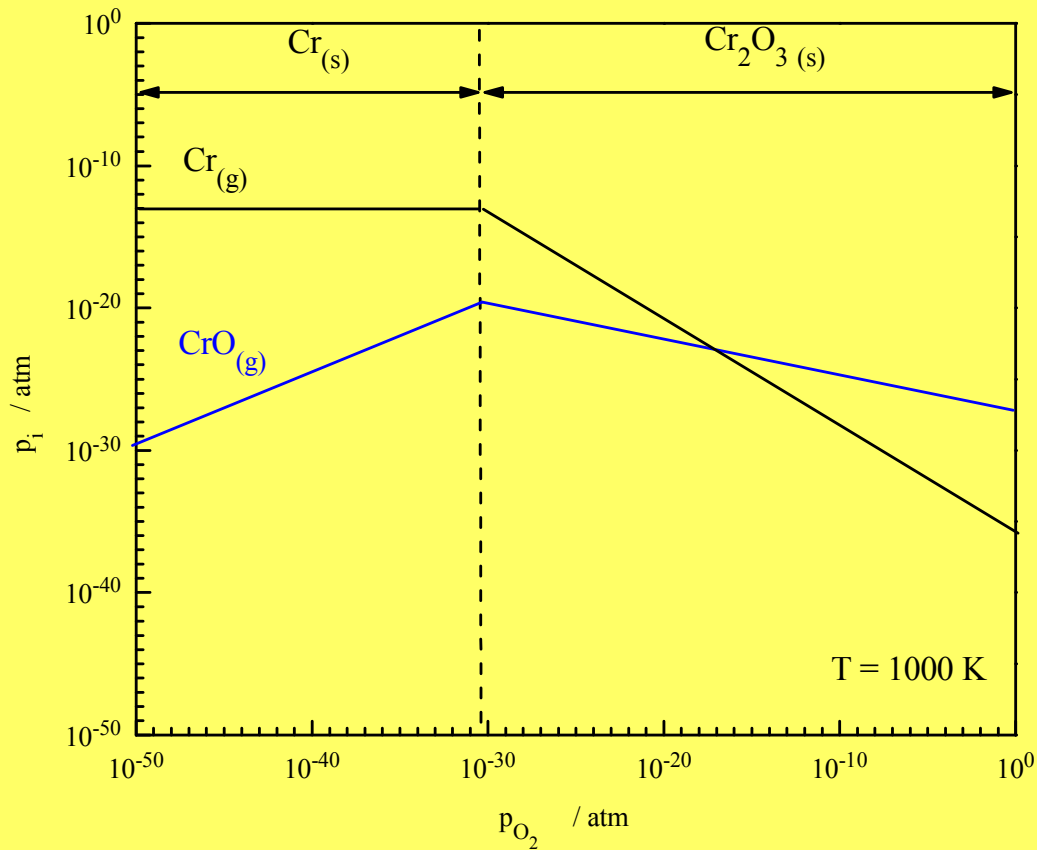


$$p_{Cr(g)} = \exp\left(-\frac{\Delta G^0}{RT}\right)$$



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

CIŚNIENIA LOTNYCH TLENKÓW

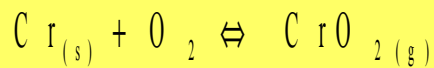
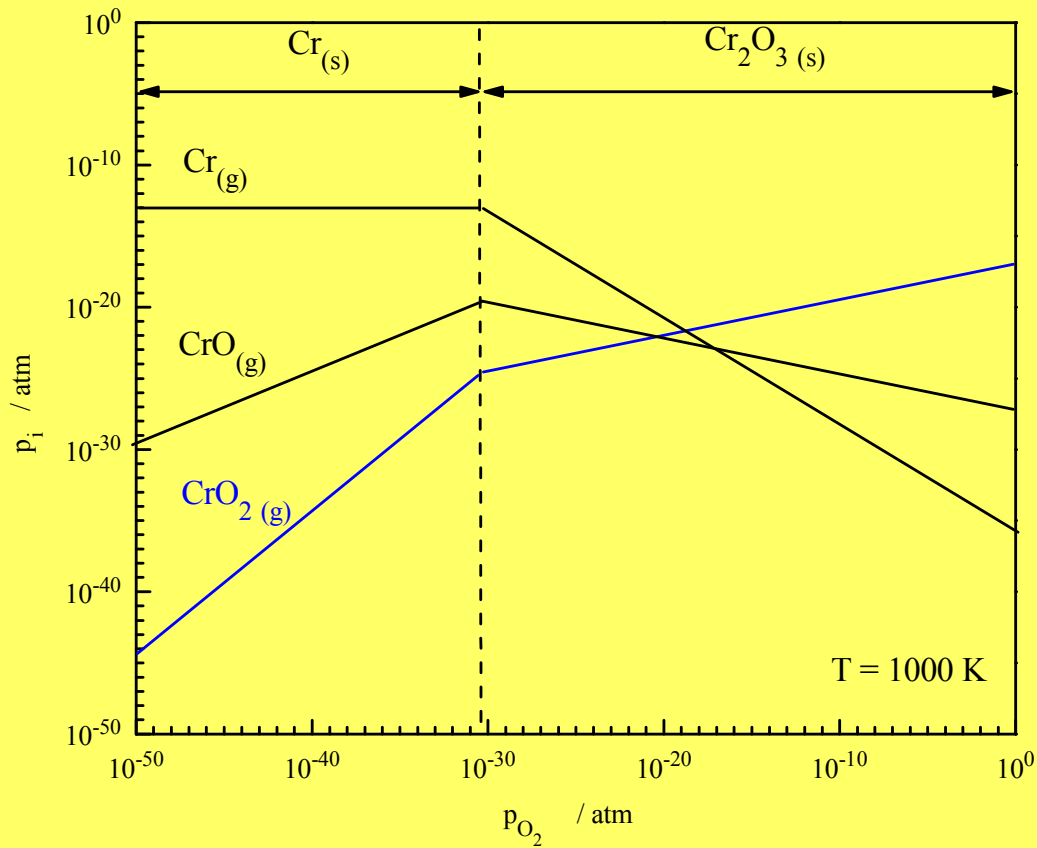


$$p_{\text{CrO}_{(g)}} = p_{\text{O}_2}^{\frac{1}{2}} \exp\left(-\frac{\Delta G^0}{RT}\right)$$

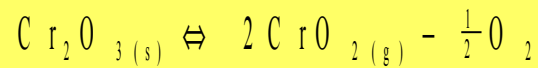


$$p_{\text{CrO}_{(g)}} = p_{\text{O}_2}^{-\frac{1}{4}} \exp\left(-\frac{\Delta G^0}{2RT}\right)$$

CIŚNIENIA LOTNYCH TLENKÓW

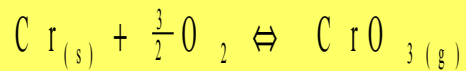
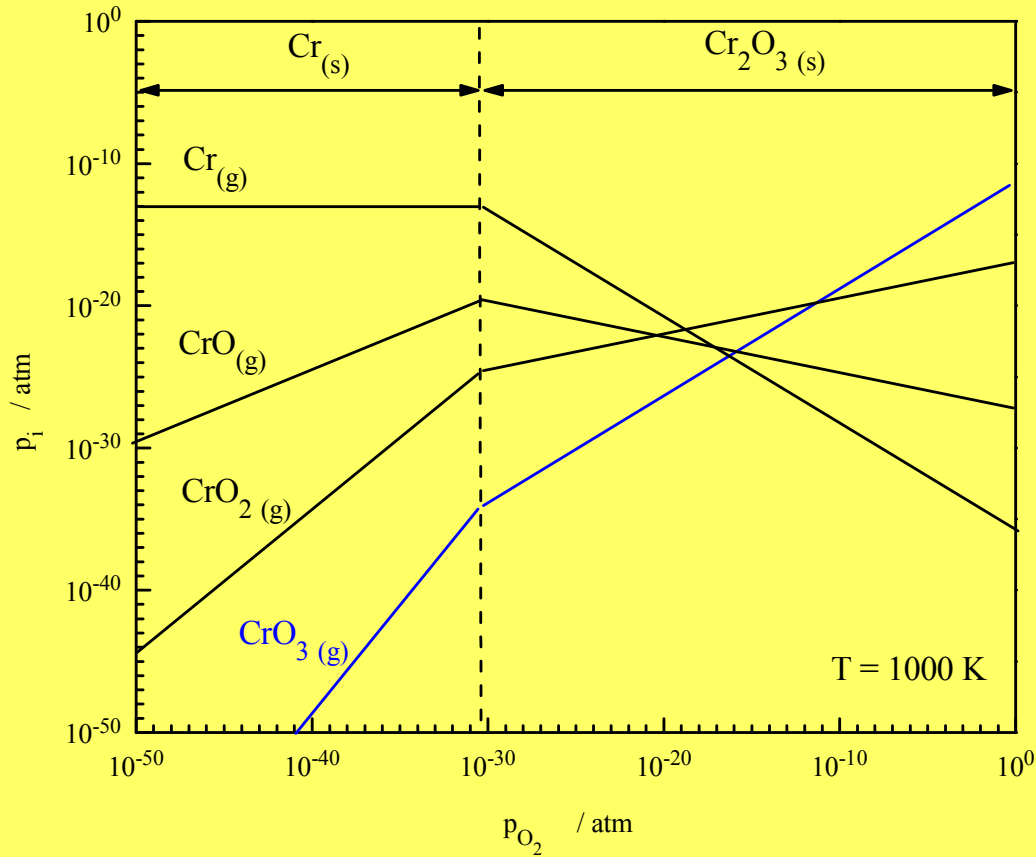


$$p_{\text{CrO}_{2(g)}} = p_{\text{O}_2} \exp\left(-\frac{\Delta G^0}{RT}\right)$$

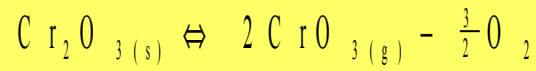


$$p_{\text{CrO}_{2(g)}} = p_{\text{O}_2}^{\frac{1}{4}} \exp\left(-\frac{\Delta G^0}{2RT}\right)$$

CIŚNIENIA LOTNYCH TLENKÓW

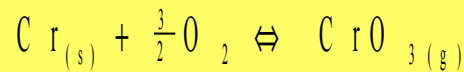
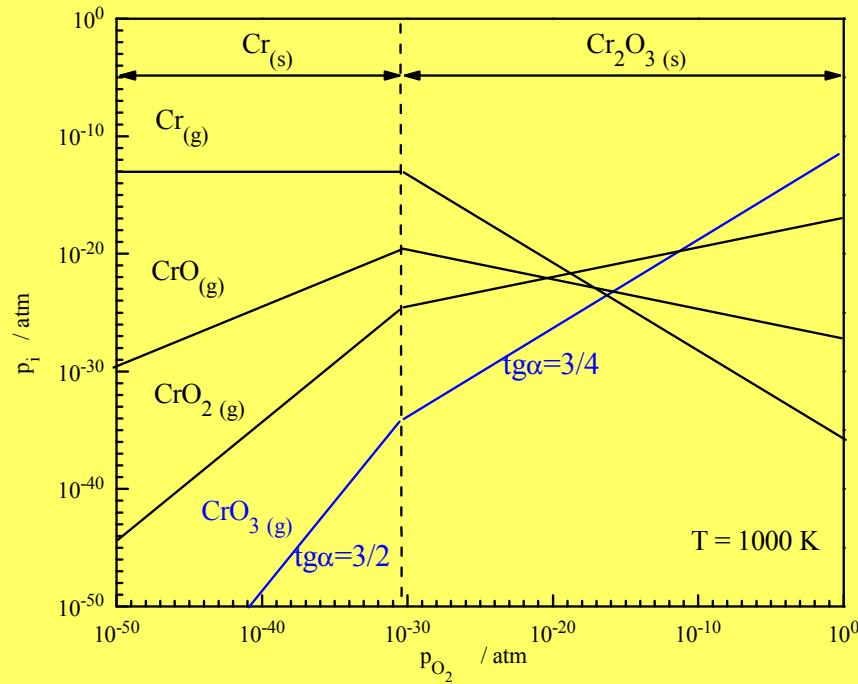


$$p_{CrO_3(g)} = p_{O_2}^{\frac{3}{2}} \exp\left(-\frac{\Delta G^0}{RT}\right)$$



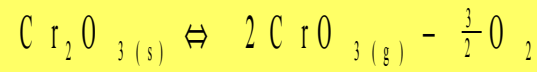
$$p_{CrO_3(g)} = p_{O_2}^{\frac{1}{4}} \exp\left(-\frac{\Delta G^0}{2RT}\right)$$

CIŚNIENIA LOTNYCH TLENKÓW



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

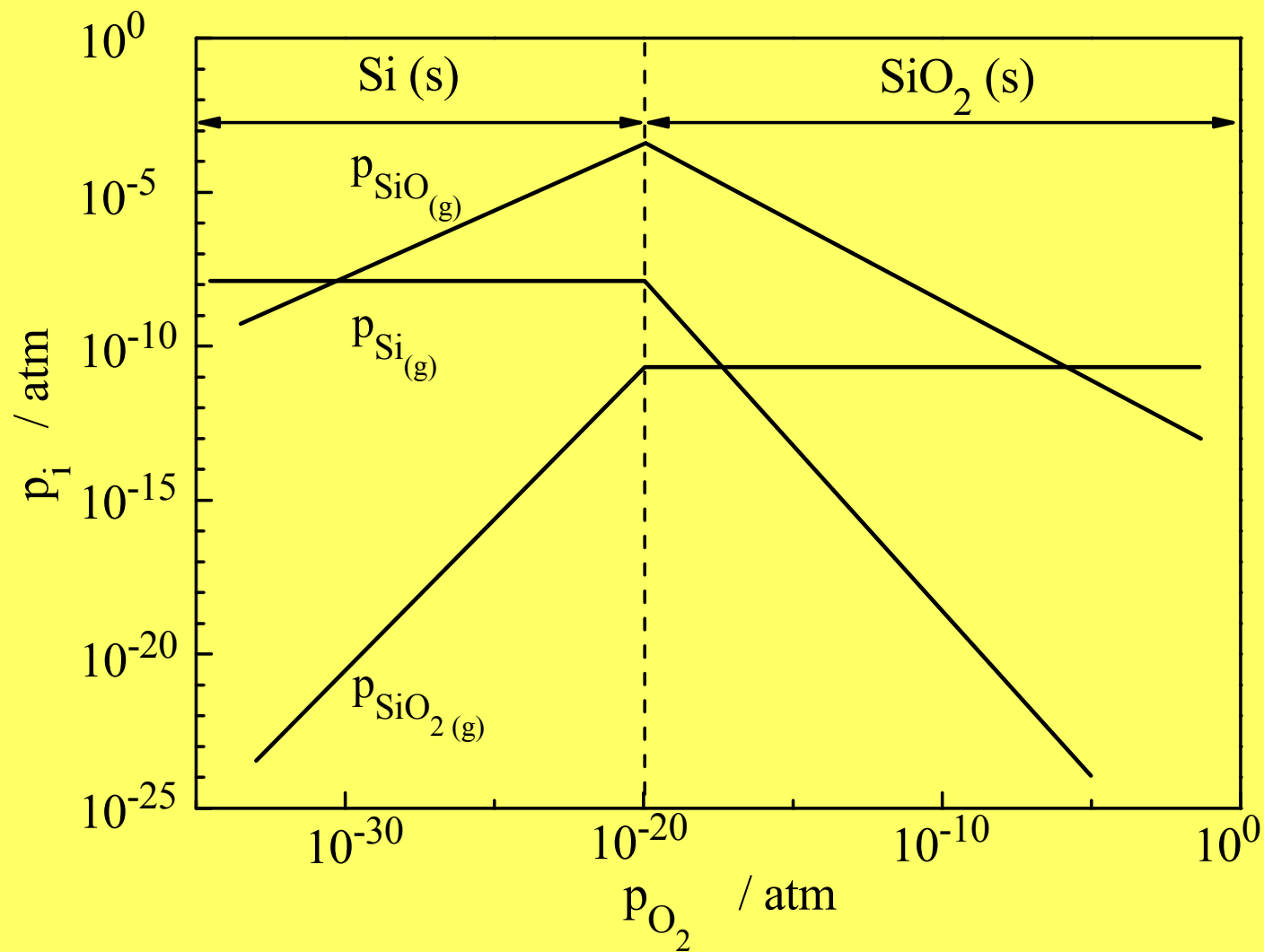
$$\log p_{\text{CrO}_{3(g)}} = \frac{3}{2} \log p_{\text{O}_2} + \log(\text{const})$$



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

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

CIŚNIENIA LOTNYCH TLENKÓW



KONIEC