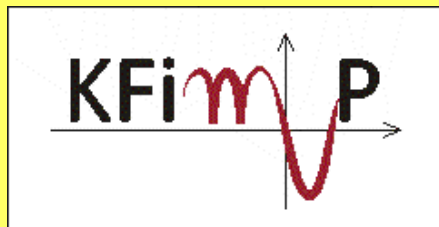


BASIC CHEMISTRY AND THERMODYNAMICS OF HIGH-TEMPERATURE MATERIALS

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Introductory remarks

Application of many materials at high temperatures requires their endurance with minimal change in their chemical composition and microstructure over long periods of time (hours to years). As the chemical reactions at high temperatures often occur fast, the equilibrium state, rather than endurance of metastable states, determines the suitability of a given material for a proposed application.

Determination of dissociation pressure



where:

Me – metal

X₂ – oxidant

MeX – product of oxidation reaction (*scale*)

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

where:

ΔG – free energy change of reaction (1)

μ_i – chemical potential of a given component

Determination of dissociation pressure

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

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)

In the case of pure substances in the solid phase:

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

In the case of substances in the gas phase:

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

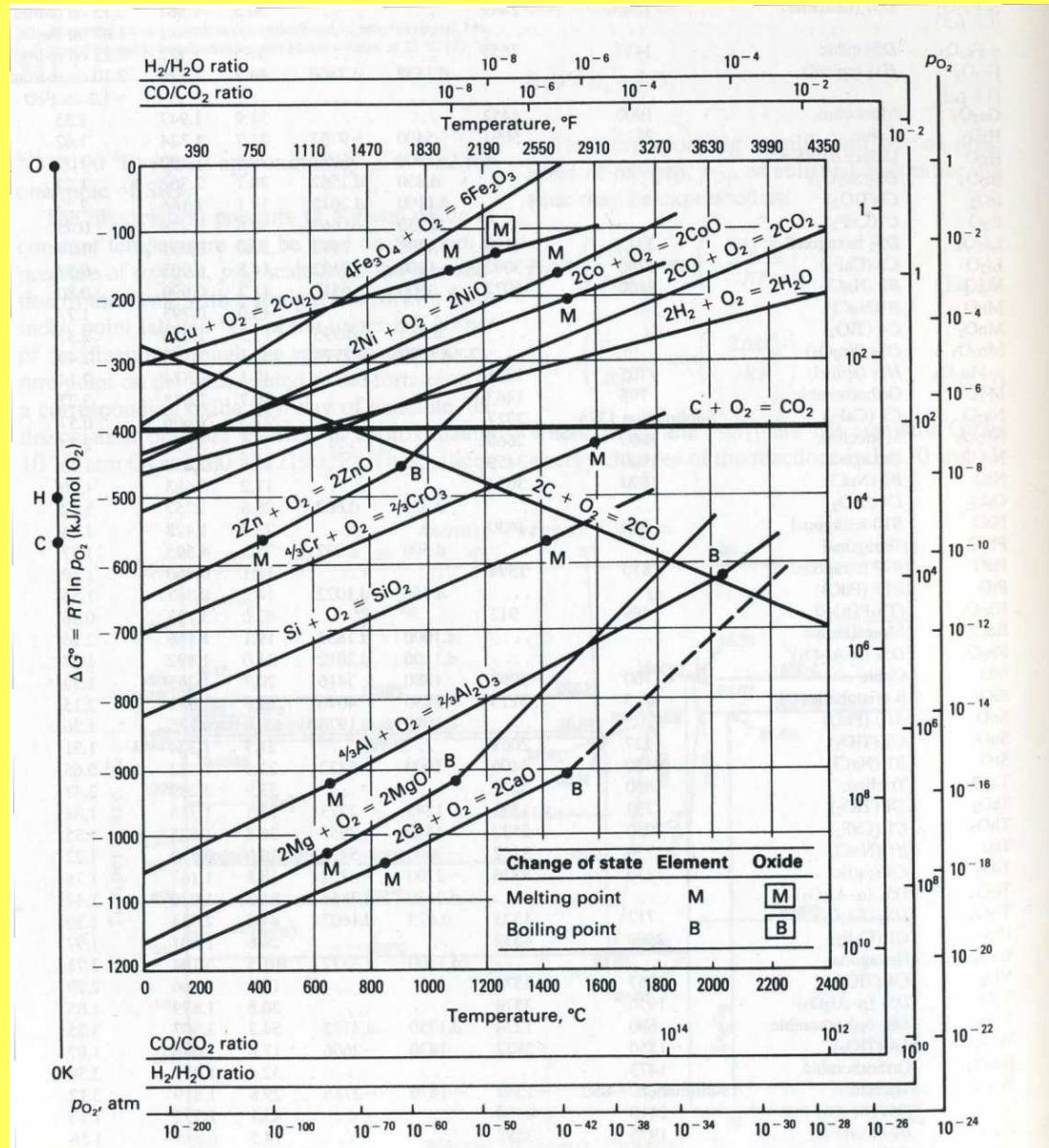
Determination of dissociation pressure

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

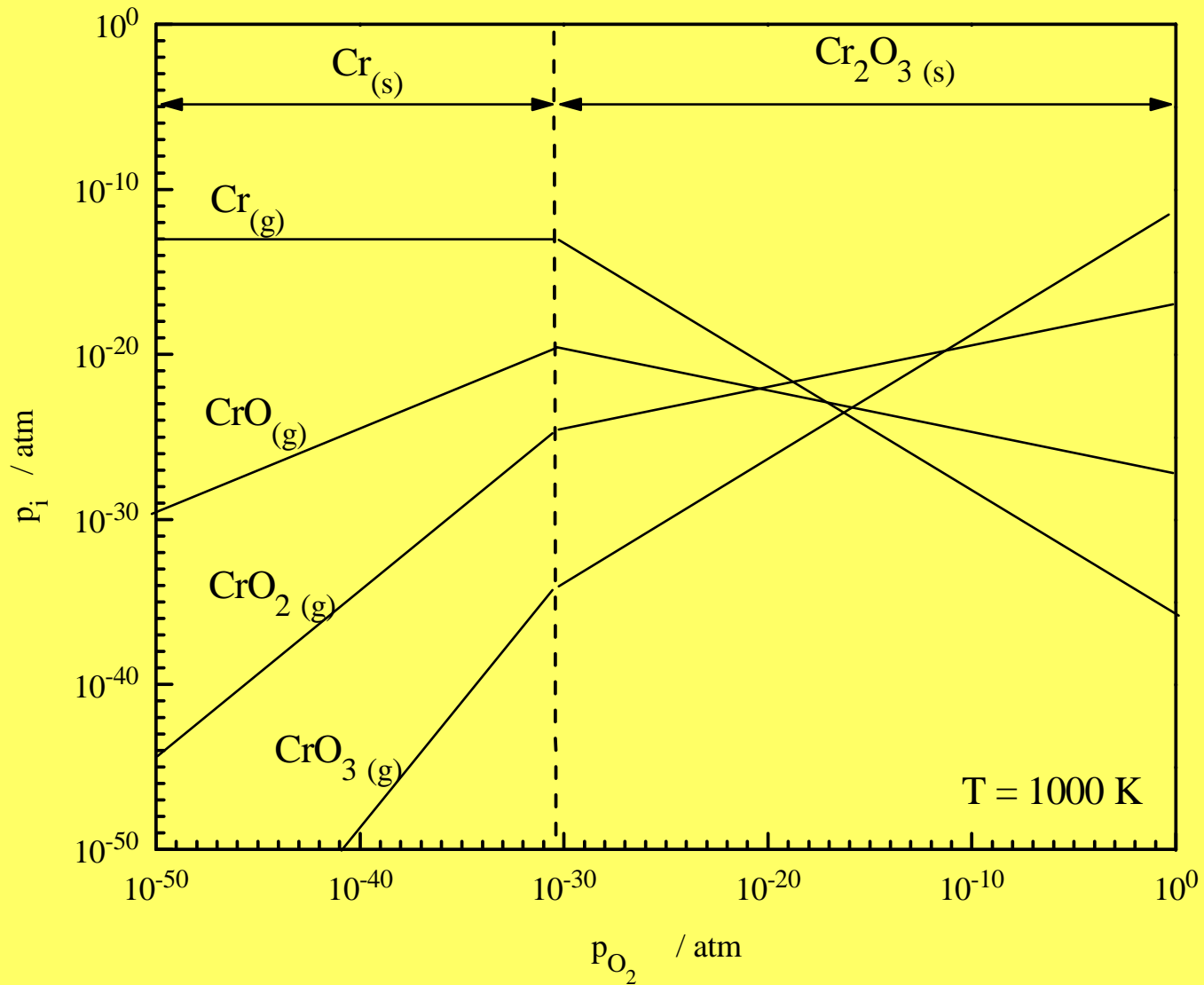
At thermodynamic equilibrium $\Delta G = 0$, and then:

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

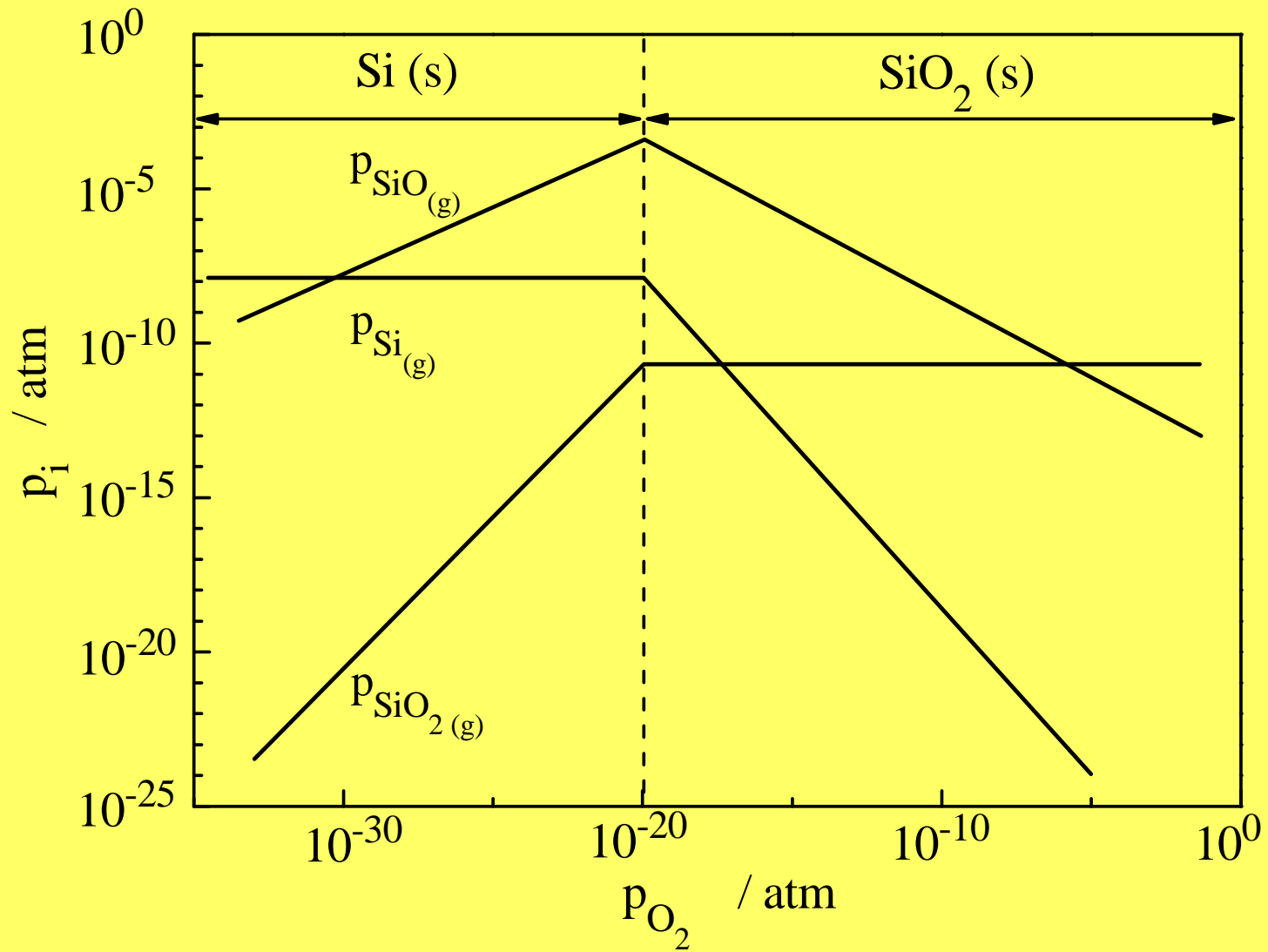
ELLINGHAM-RICHARDSON DIAGRAM (RICHARDSON-JEFFES)



PRESSURES OF VOLATILE OXIDES



PRESSURES OF VOLATILE OXIDES



Modes of materials degradation at high temperatures

- melting and softening (high melting compounds required for HT)
- vaporization (sublimation)
- diffusion and solid state reactions
- solid-solid phase transformations
- corrosion and chemical reaction with the ambient atmosphere

Selected properties of metal oxides

<i>Oxide</i>	<i>Structure</i>	<i>Melting point, °C</i>	<i>Boiling point, °C</i>	<i>Molar volume, cm³</i>	<i>Volume ratio (oxide/metal)</i>
α -Al ₂ O ₃	D5 ₁ (corundum)	2015	2980	25.7	1.28
γ -Al ₂ O ₃	(defect spinel)	$\gamma \rightarrow \alpha$...	26.1	1.31
BaO	B1 (NaCl)	1923	~2000	26.8	0.69
BaO ₂	Tetragonal (CaC ₂)	450	d.800	34.1	0.87
BeO	Br (ZnS)	2530	~3900	8.3	1.70
CaO	B1 (NaCl)	2580	2850	16.6	0.64
CaO ₂	CII (CaC ₂)	...	d.275	24.7	0.95
CdO	B1 (NaCl)	~1400	d.900	18.5	1.42
Ce ₂ O ₃	D5 ₂ (La ₂ O ₃)	1692	...	47.8	1.15
CeO ₂	CI (CaF ₂)	~2600	...	24.1	1.17
CoO	B1 (NaCl)	1935	...	11.6	1.74
Co ₂ O ₃	Hexagonal	...	d.895	32.0	2.40
Co ₃ O ₄	HI ₁ (spinel)	→ CoO	...	39.7	1.98
Cr ₂ O ₃	D5 ₁ (α -Al ₂ O ₃)	2435	4000	29.2	2.02
Cs ₂ O	Hexagonal (CdCl ₂)	...	d.400	66.3	0.47
Cs ₂ O ₃	Cubic (Th ₃ P ₄)	400	650	70.1	0.50
CuO	B26 monoclinic	1326	...	12.3	1.72
Cu ₂ O	C3 cubic	1235	d.1800	23.8	1.67
FeO	B1 (NaCl)	!420	...	12.6	1.78 on α -iron
α -Fe ₂ O ₃	D5 ₁ (Haematite)	1565	...	30.5	2.15 on α -iron
γ -Fe ₂ O ₃	D5 ₇ cubic	1457	...	31.5	2.22 on α -iron
Fe ₃ O ₄	HI ₁ (spinel)	...	d. 1538	44.7	2.10 on α -iron
Ga ₂ O ₃	Monoclinic	1900	...	31.9	1.35
HfO ₂	Cubic	2812	~5400	21.7	1.62

Selected properties of metal oxides

<i>Oxide</i>	<i>Structure</i>	<i>Melting point, °C</i>	<i>Boiling point, °C</i>	<i>Molar volume, cm³</i>	<i>Volume ratio (oxide/metal)</i>
In ₂ O ₃	D5 ₃ (Sc ₂ O ₃)	...	d.850	38.7	1.23
IrO ₂	C4 (TiO ₂)	...	d.1100	19.1	2.23
La ₂ O ₃	D5 ₃ (Sc ₂ O ₃)	...	d.850	38.7	1.23
Li ₂ O	Cl (CaF ₂)	~1700	1200	14.8	0.57
MgO	B1 (NaCl)	2800	3600	11.3	0.80
MnO	B1 (NaCl)	13.0	1.77
MnO ₂	C4 (TiO ₂)	...	d.535	17.3	2.37
Mn ₂ O ₃	D5 ₃ (Sc ₂ O ₃)	...	d.1080	35.1	2.40
Mn ₃ O ₄	Hl ₁ (spinel)	1705	...	47.1	2.14
MoO ₃	Orthorhombic	795	...	30.7	3.27
Na ₂ O	Cl (CaF ₂)	Subl. 1275	...	27.3	0.57
Nb ₂ O ₅	Monoclinic	1460	...	59.5	2.74
Nd ₂ O ₃	Hexagonal	~1900	...	46.5	1.13
NiO	B1 (NaCl)	1990	...	11.2	1.70
PbO	B10 tetragonal	888	...	23.4	1.28
Pb ₃ O ₄	Tetragonal	...	d.500	75.3	1.37
PdO	B17 tetragonal	870	...	14.1	1.59
PtO	B17 (PdO)	...	d.550	14.2	1.56
Rb ₂ O ₃	(Th ₃ P ₄)	489	...	62.0	0.56
ReO ₂	Monoclinic	...	d.1000	19.1	2.16
Rh ₂ O ₃	D5 ₁ (α -Al ₂ O ₃)	...	d.1100	31.0	1.87
SiO	Cubic	~1700	1880	20.7	1.72

Selected properties of metal oxides

<i>Oxide</i>	<i>Structure</i>	<i>Melting point, °C</i>	<i>Boiling point, °C</i>	<i>Molar volume, cm³</i>	<i>Volume ratio (oxide/metal)</i>
SiO ₂	β cristobalite C9	1713	2230	25.9	2.15
SnO	B10 (PbO)	...	d.1080	20.9	1.26
SnO ₂	C ₄ (TiO ₂)	1127	...	20.9	1.26
SrO	B1 (NaCl)	2430	~3000	22.0	0.65
Ta ₂ O ₅	Triclinic	1800	...	53.9	2.47
TeO ₂	C ₄ (TiO ₂)	733	1245	28.1	1.38
ThO ₂	C1 (CaF ₂)	3050	4400	26.8	1.35
TiO	B1 (NaCl)	1750	~3000	13.0	1.22
TiO ₂	C4 (Rutile)	1830	~2700	18.8	1.76
Ti ₂ O ₃	D5 ₁ (α-Al ₂ O ₃)	...	d.2130	31.3	1.47
Tl ₂ O ₃	D5 ₃ (Sc ₂ O ₃)	717	d.875	44.8	1.30
UO ₂	C1 (CaF ₂)	2500	...	24.6	1.97
U ₃ O ₈	Hexagonal	...	d.1300	101.5	2.71
VO ₂	C4 (TiO ₂)	1967	...	19.1	2.29
V ₂ O ₃	D5 ₁ (α-Al ₂ O ₃)	1970	...	30.8	1.85
V ₂ O ₅	D8 ₇ Orthorhombic	690	d.1750	54.2	3.25
WO ₂	C4 (TiO ₂)	~1550	~1430	17.8	1.87
B-WO ₃	Orthorhombic	1473	...	32.4	3.39
W ₂ O ₅	Triclinic	Sub.~850	~1530	29.8	3.12
Y ₂ O ₃	D5 ₃ (Sc ₂ O ₃)	2410	...	45.1	1.13
ZnO	B3 (wurtzite)	1975	...	14.5	1.58
ZrO ₂	C4 ₃ monoclinic	2715	...	22.0	1.57

Melting and boiling points of some representative metals and oxides

Materials	Approximate Melting Point (°C)	Approximate Boiling or Decomposition Point (°C)
Mo	2610	5560
MoO ₃	795	1155
W	3407	5727
WO ₃ [†]	1470	1700
Pt	1772	3800
PtO	—	d.550
PtO ₂	—	d.650
IrO ₂	—	d.1124
Rh	1966	3727
Rh ₂ O ₃	—	d.1100
Si	1414	3250
SiO	1700	1880
SiO ₂	1600	2230

[†] Significantly volatile at 800–1000°C.

Noble metals

Noble metals are used as materials for thermocouples, electrodes and crucibles at high temperatures. Noble metals, in fact, are chemically reactive under a variety of conditions, sometimes with disastrous consequences. Platinum, for example, can be seriously corroded by basic oxides, such as Na_2O and K_2O , especially when these compounds melt. The formation of an eutectic in the Pt-Si system is also a potential hazard. There are a number of binary and ternary noble metal oxides, the stability of which is generally limited to temperatures below about 1150°C . One of the greatest disadvantages of noble metals is their high price.

Binary and ternary platinum oxides

Binary and Ternary Platinum Oxides

Oxide	Decomposition Temperature (°C)
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PtO	555
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OsO ₄	Boils at 130
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IrO ₂	1100
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RhO ₂	1127
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RhO	1120
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Rh ₂ O ₃	880
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PtO ₂	430
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Pb ₂ PtO ₄	735
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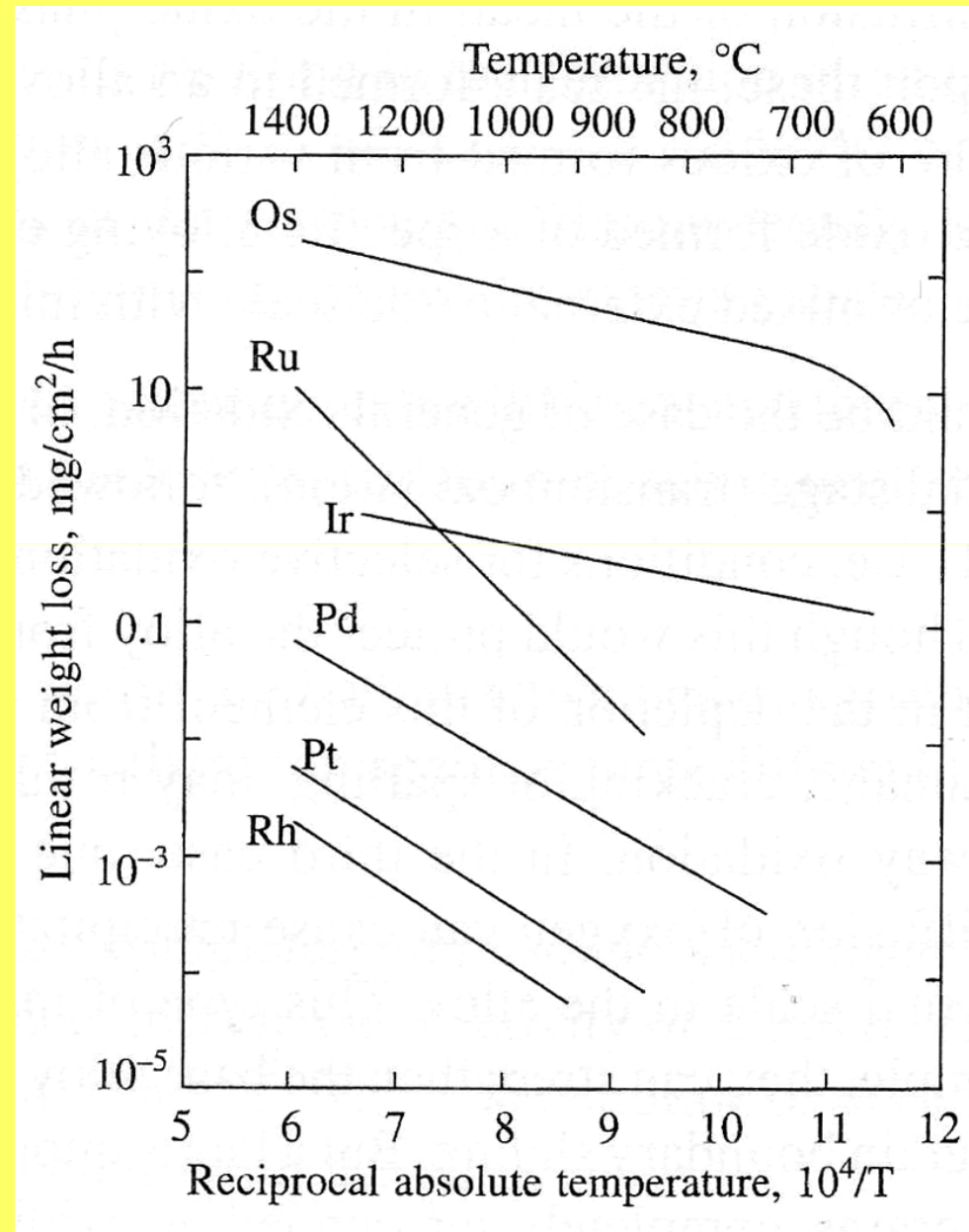
PbPt ₂ O ₄	750
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Ca ₂ Pt ₃ O ₈	720
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Noble metal eutectics (°C) with selected elements

Element	Pt	Rh	Ir
B	825	1131	1046
P	588	1254	1262
Si	890	1389	1470
Sn	1070	—	—
Pb	327	—	—
Bi	730	—	—
Sb	633	—	—
As	597	—	—

Evaporation rate of noble metals as a function of temperature



Properties of standard thermocouples

Type	Base Composition	Melting Point (°C)	Ambient	Temperature Range (°C)
J	Fe (+)	1400	Oxidizing or reducing	7–600 ^a
	44Ni-55Cu(-)	1210		
K	90Ni-9Cr(+)	1350	Oxidizing	-270–1372 ^a
	94Ni-Al,Mn, Si, Fe, Co(-)	1400		
N	84Ni-14Cr-1.4Si(+)	1410	Oxidizing	-270–1260 ^a
	95Ni—4.4Si-0.15 Mg(-)	1400		
T	Cu(+)	1083	Oxidizing	-200–370 ^a
	44Ni-55Cu(-)	1210		
E	90Ni-9Cr(+)	1350	Oxidizing	-200–870 ^a
	44Ni-55Cu(-)	1210		
R	87Pt-13Rh(+)	1860	Oxidizing or inert	-50–1768
	Pt(-)	1769		
S	90Pt-10Rh(+)	1769	Oxidizing or inert	-50–1768
	Pt(-)	1927		
B	70Pt-30Rh(+)	1927	Oxidizing, vacuum, or inert	800–1820
	94Pt-6Rh(-)	1826		
C	W-5Re (+)	3350	Inert	0–2760 ^a
	W-26Re (-)	3120		

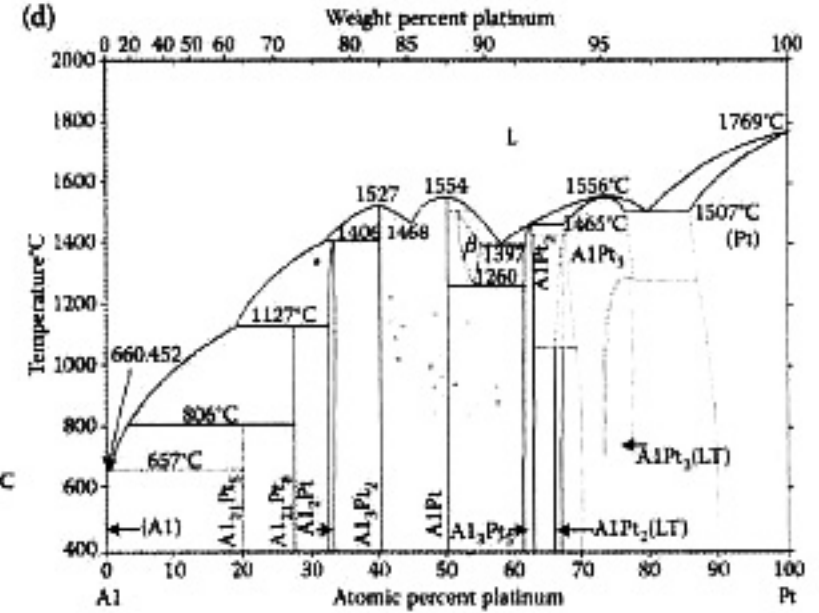
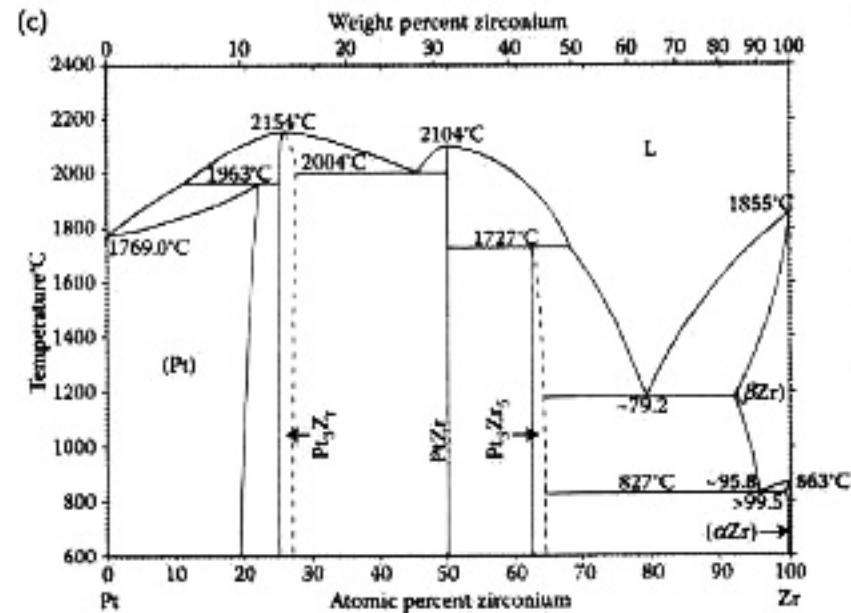
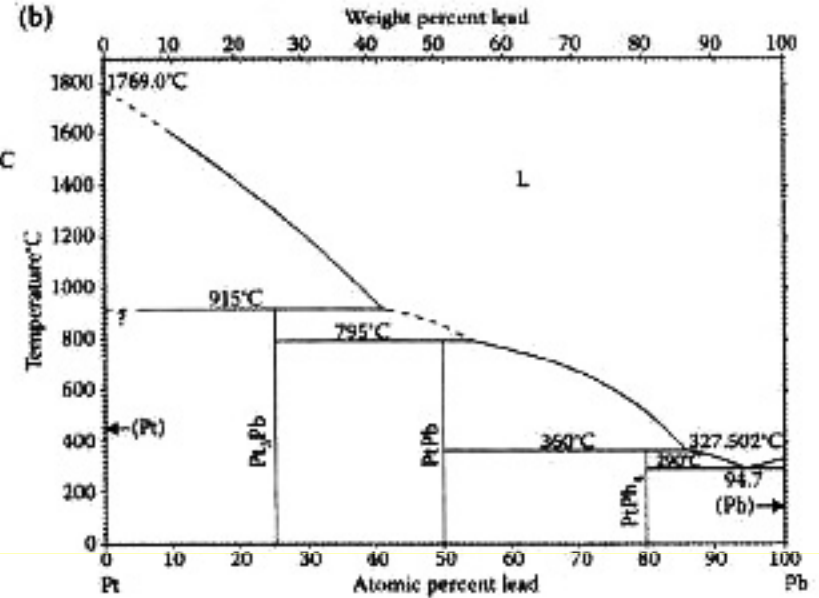
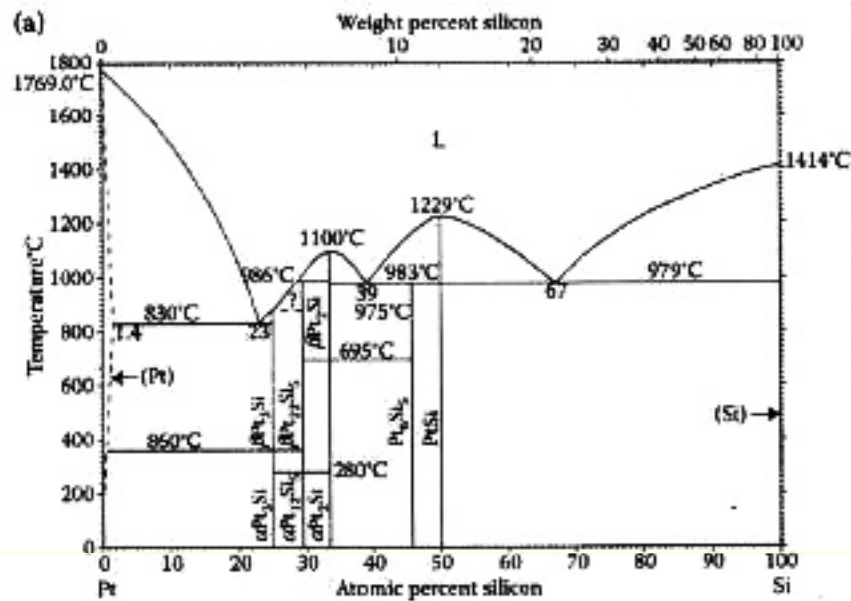
Source: Davis, J. R. *ASM Specialty Handbook: Heat-Resistant Materials*, ASM International. ISBN: 0871705966, 1997, pp. 1–591–51. From Springer Science+Business Media: *Materials Handbook: A Concise Desktop Reference*, 1st Edition, 2000, pp. 1–595, Cardarelli, F.

^a Use in oxidizing atmospheres limited by easy oxidation of the metals, may be used somewhat higher in inert atmospheres, but wires become very brittle on heating.

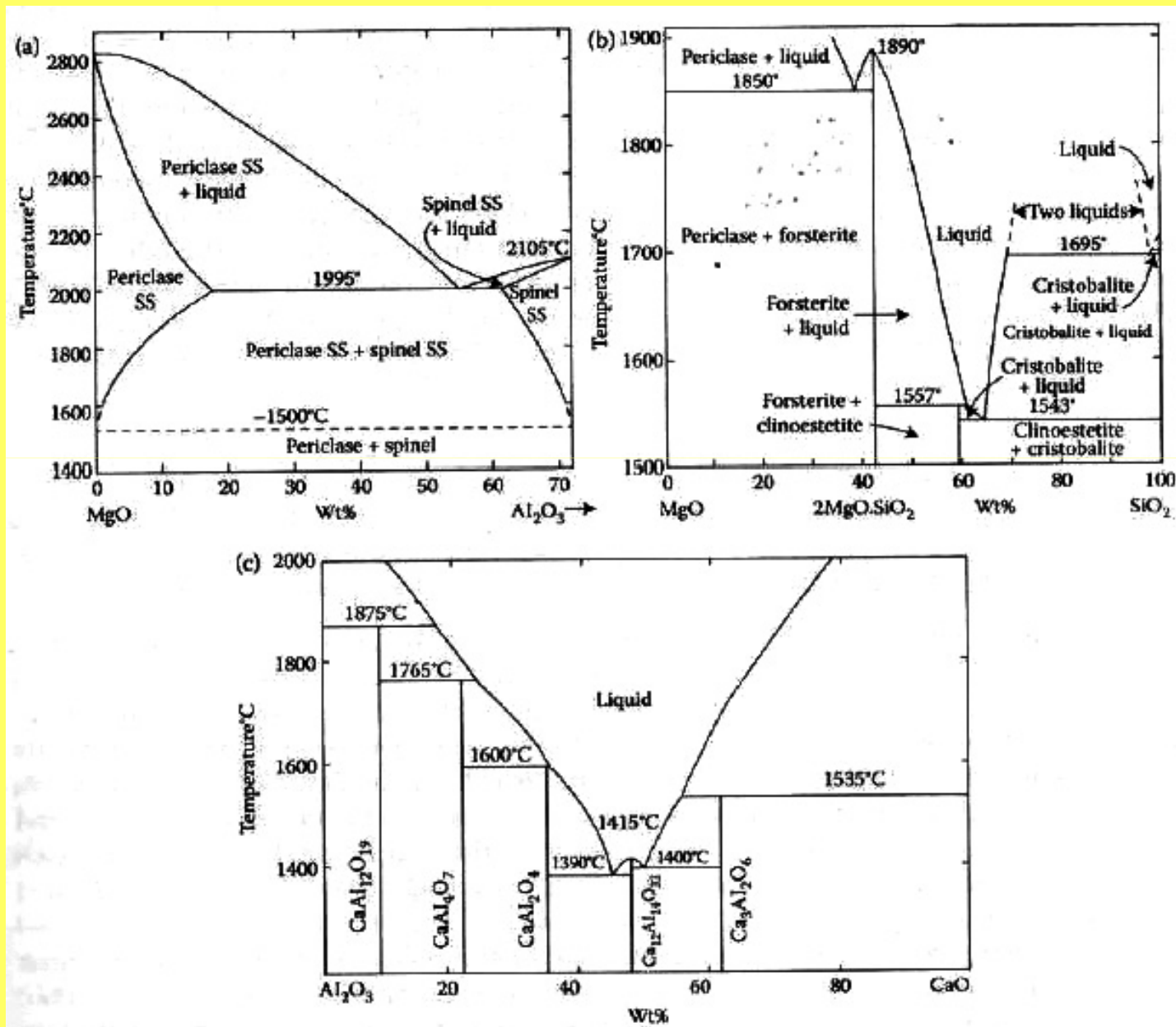
HT materials used above 2000°C

In the absence of oxygen, refractory metals and some of their compounds can be used up to temperatures of about 2000°C, encountering neither melting nor serious vaporization. They can be used in a vacuum or in an inert noble gas, but not in nitrogen because of potential nitride formation. However these metals can be easily oxidized and their oxides, in contrast, melt and boil in the 800-1000°C temperature range. Graphite can be used up to about 2200°C.

HT materials used above 2000°C



HT materials used above 2000°C



Phase transitions of some refractory oxides

Oxide	Phase Transition	Transition Temperature (°C)	Enthalpy of Transition kJ.mole ⁻¹	Entropy of Transition J mol ⁻¹ K ⁻¹
ZrO ₂	m-t	1202	5.4 ± 0.3	3.7 ± 0.3
	t-c	2300	4.2 ± 0.5	1.6 ± 0.2
	m-c	Metastable	9.6	5.3
HfO ₂	m-t	1650	32.5 ± 1.7	
	t-c	2700		
	m-c	Metastable		
Y ₂ O ₃	C-c	2200 ± 50	24 ± 5	
SiO ₂ (Stevens et al., 1997; Roy and Roy, 1964; Richet et al., 1982; Navrotsky et al., 1980)	Quartz-	870	1.32	
	tridymite	1473 ± 30	0.96 ± 0.25	
	tridymite-cristobalite	525	9.49 ± 0.25	
	cristobalite	835	10.20 ± 0.33	
	α-β	1427		
	cristobalite- quartz	1726		
	amorphous SiO ₂			
	-quartz amorphous SiO ₂ -cristobalite			

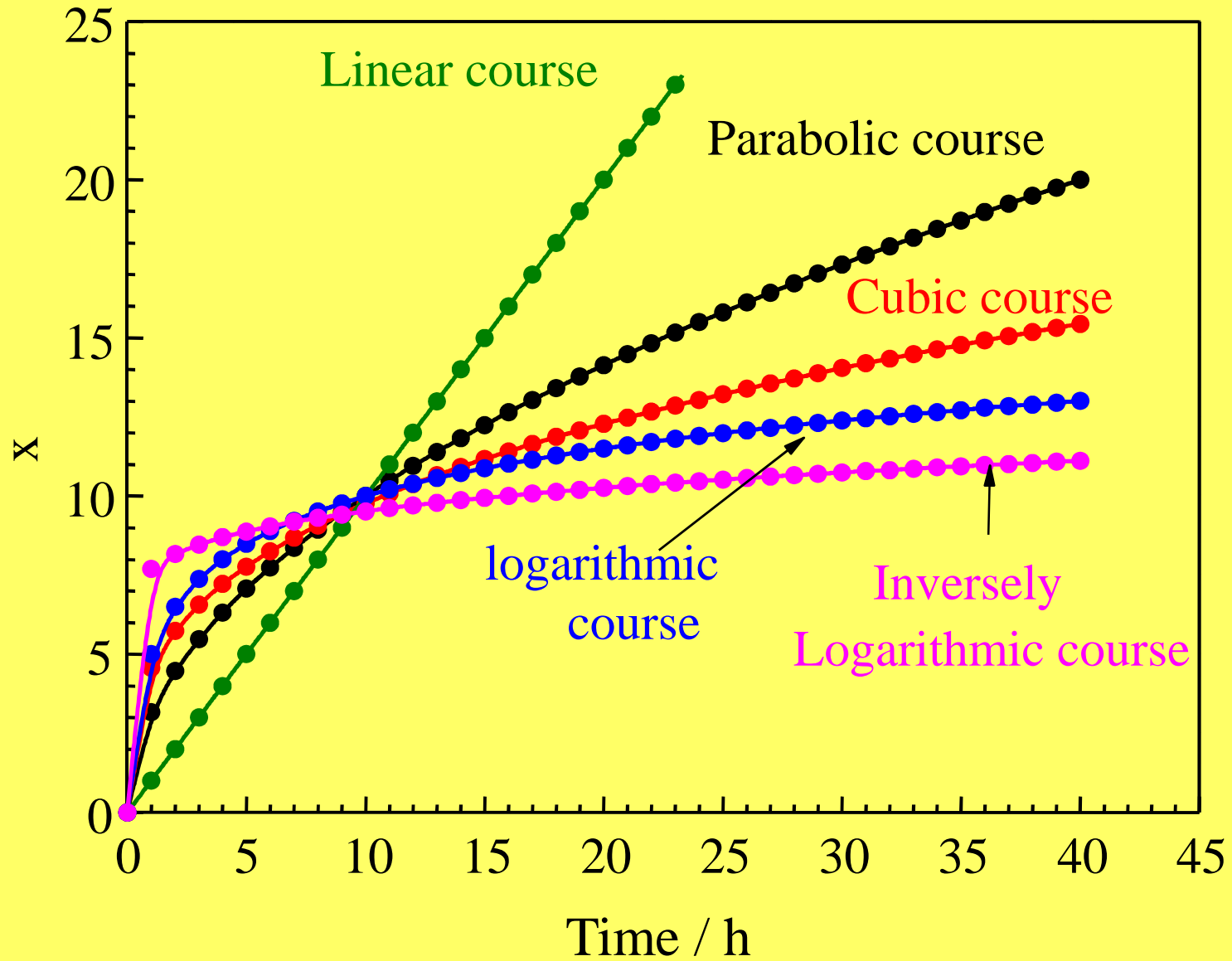
Source: Navrotsky, A., *Journal of Materials Chemistry*, 15(19), 2005, 1883–1890.

Note: M, monoclinic; t, tetragonal; c, cubic fluorite; C, cubic C-type (ordered vacancy).

RATE LAWS OF METALS OXIDATION

- The linear law
- The parabolic law
- The cubic law
- The paralinear law
- The logarithmic law
- The inversely logarithmic law

RATE LAWS OF METALS OXIDATION



RATE LAWS OF METALS OXIDATION

The parabolic law

The slowest partial process determined by the rate of scale formation is diffusion transport of substrates through compact layer of reaction products (scale) formed on metal surface.

$$\frac{dx}{dt} = \frac{k'_p}{x} \quad x^2 = 2k'_p \cdot t + C \quad \text{The Tammann Equation (1920)}$$

- x – scale thickness [cm]
- t – reaction time [s]
- k'_p – parabolic oxidation rate constant [cm²·s⁻¹]
- C – integration constant [cm²]

KINETICS LAWS OF METALS OXIDATION

The parabolic law

$$\frac{d\left(\frac{\Delta m}{S}\right)}{dt} = \frac{k_p}{\frac{\Delta m}{S}} \quad \left(\frac{\Delta m}{S}\right)^2 = k_p \cdot t + C \quad \text{Pilling-Bedworth Equation (1923)}$$

Δm – sample weight change [g]

t – reaction time [s]

k_p – parabolic oxidation rate constant [$\text{g}^2 \cdot \text{cm}^{-4} \cdot \text{s}^{-1}$]

C – integration constant [$\text{g}^2 \cdot \text{cm}^{-4}$]

S – sample surface [cm^2]

$$\frac{\Delta m}{S} \rightarrow 0 \Rightarrow \frac{d\left(\frac{\Delta m}{S}\right)}{dt} \rightarrow \infty$$

KINETICS LAWS OF METALS OXIDATION

The relationship between k_p and k'_p

$$k_p = 2 \left(\frac{M_o}{\bar{V} \cdot Z_o} \right)^2 k'_p$$

where:

k_p – parabolic oxidation rate constant [$\text{g}^2\text{cm}^{-4}\text{s}^{-1}$]

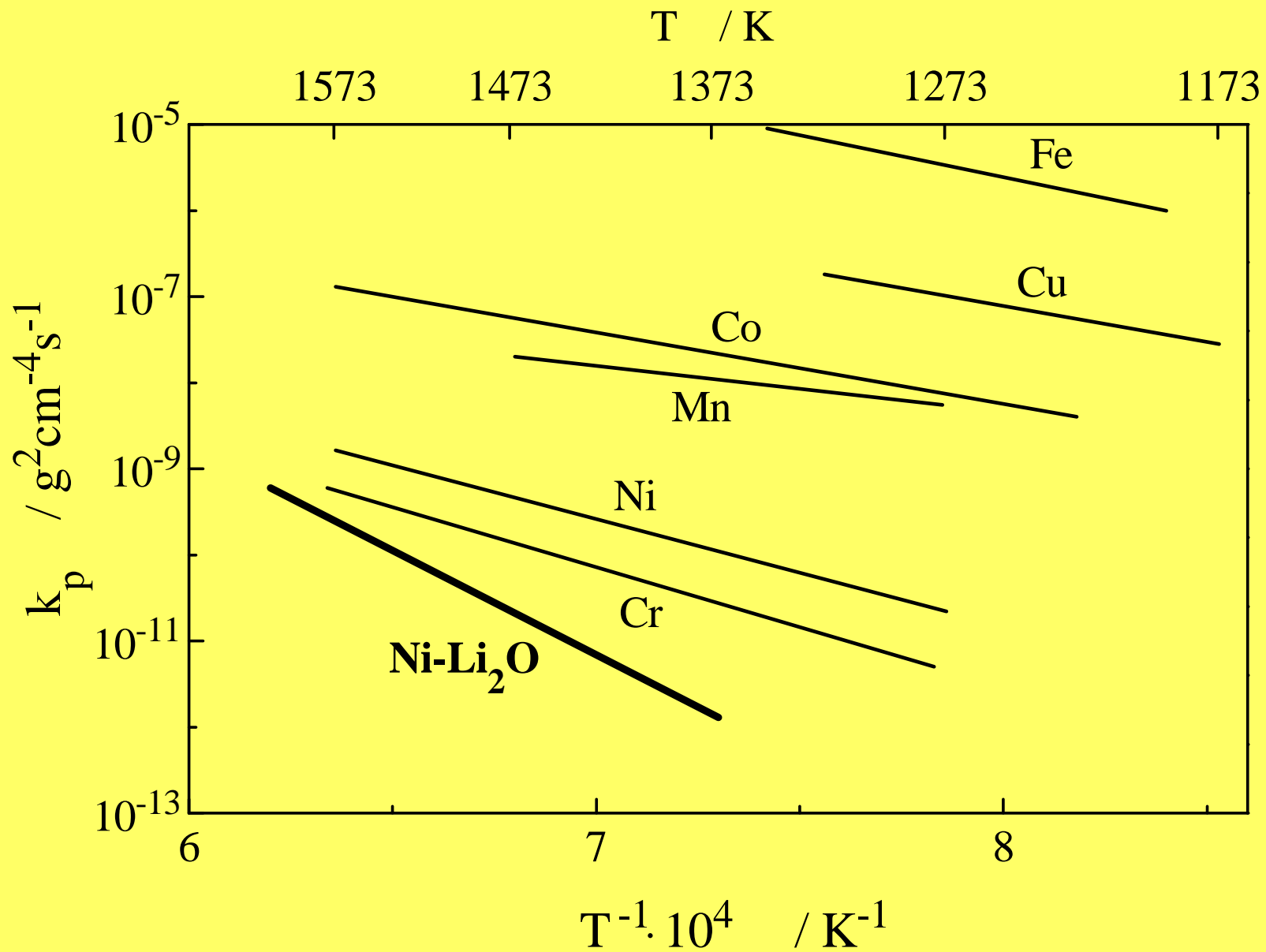
k'_p – parabolic oxidation rate constant [cm^2s^{-1}]

\bar{V} – equivalent volume of scale formed compound (e.g. oxide)

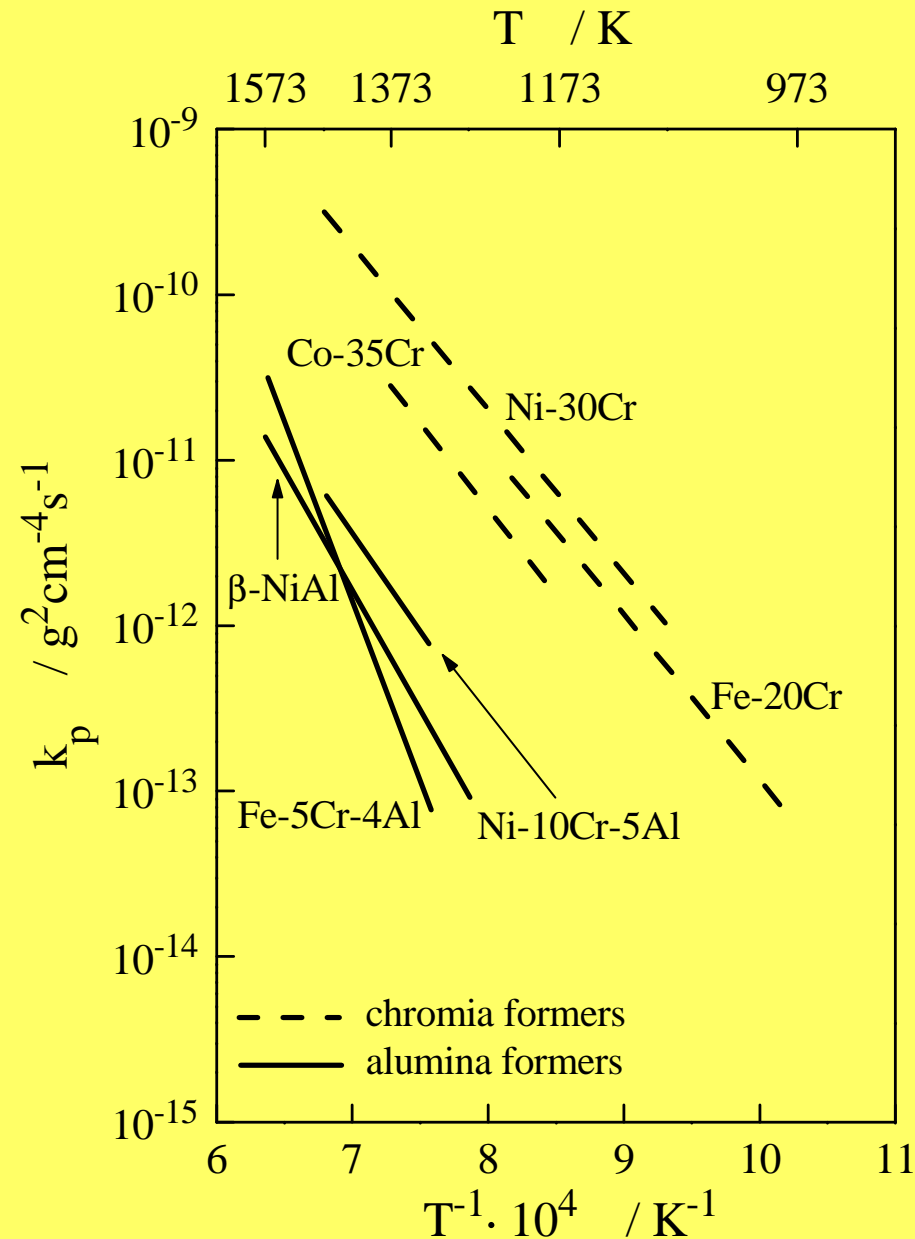
M_o – atomic mass of oxidant (e.g. oxide)

Z_o – valency of oxidant anions in the scale

Oxidation rate of selected metals



Oxidation rate of selected alloys

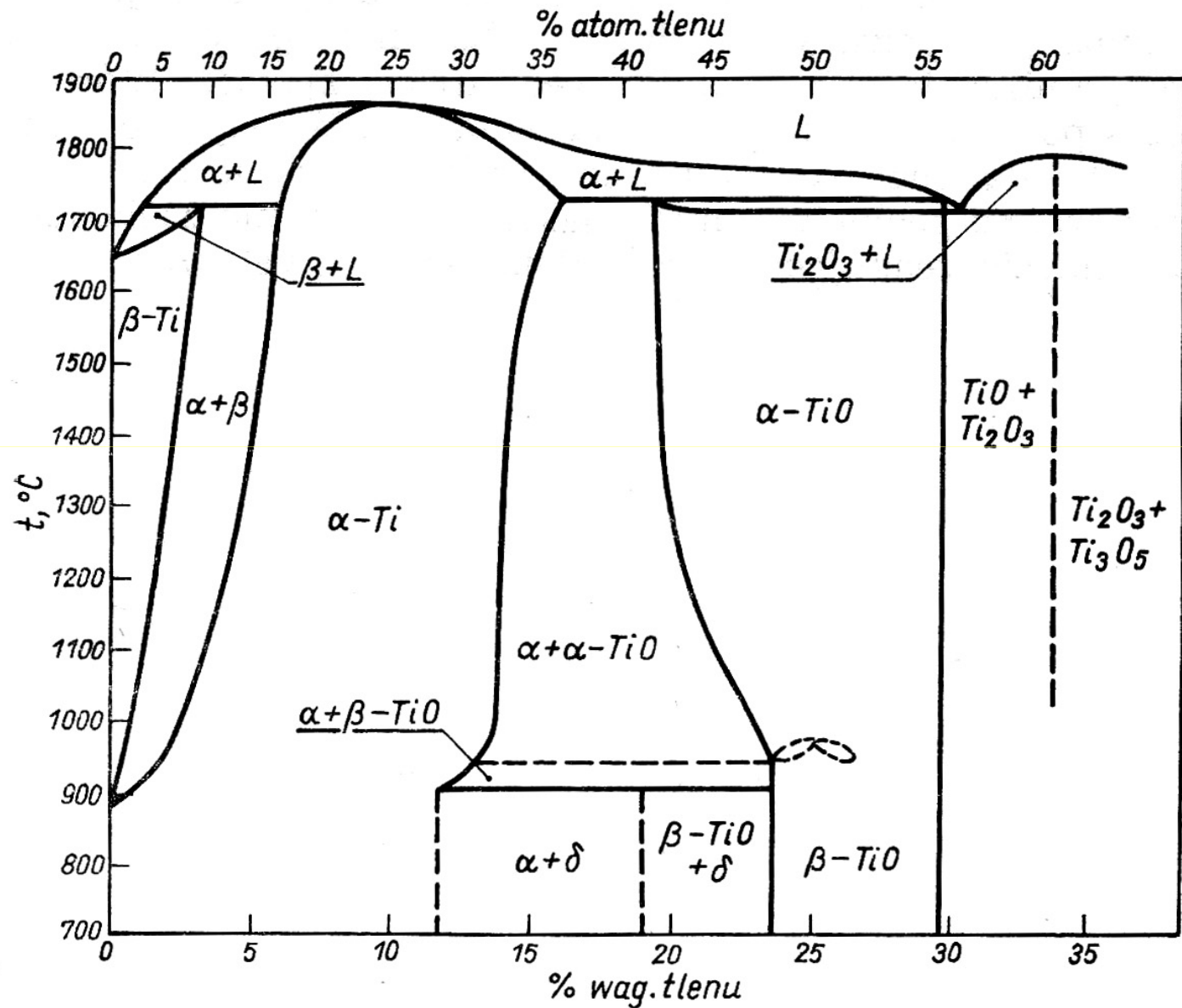


Oxidation course of selected metals

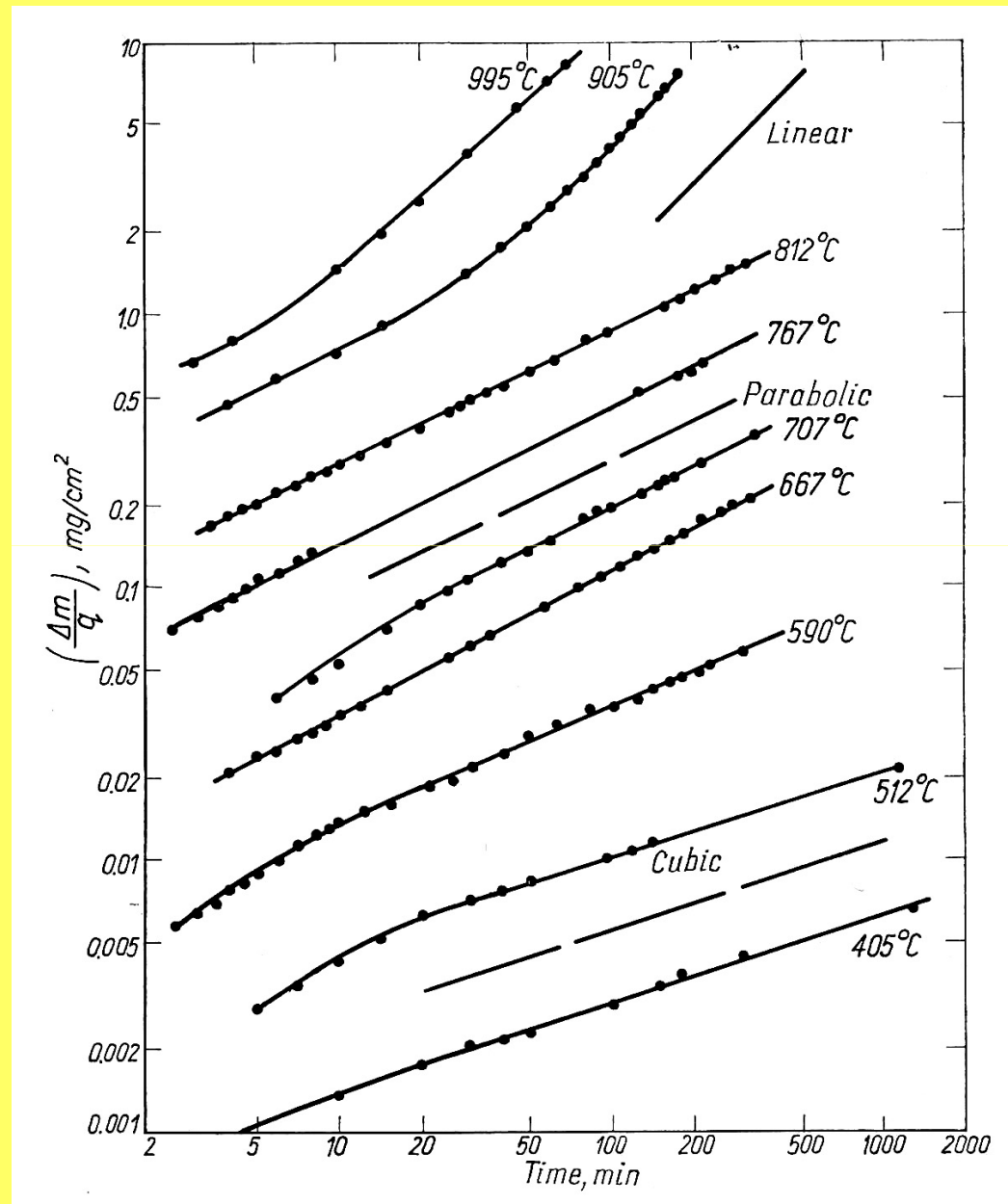
Metal	Temperature, °C											
	100	200	300	400	500	600	700	800	900	1000	1100	
Mg	log.		par.		paralin.		lin.					
Ca	log.			par.	lin.		lin.					
Ce	log.	lin.	incr.									
Th			par.		lin.		lin.					
U	par.	paralin.	lin.	incr.								
Ti			log.		cu.		cu.	paralin.		paralin.		
Zn			log.	cu			cu.		cu.	cu.	lin.	
Nb			par.	par.		paralin.		lin.	lin.		incr.	
Ta	log.	inv. log.		par.		paralin.		lin.		lin.		
Mo			par.		paralin.		paralin.	lin.		lin.		
W				par.			par.	paralin.		paralin.		paralin.
Fe	log.	log.	par.	par.		par.		par.		par.		par.
Ni		log.	log.	cu.		par.				par.		par.
Cu		log.	cu.	cu.		par.		par.				
Zn		log		log.	par.							
Al	log.	inv. log.	log.	log.	par.		lin.					
Ge					par.			paralin.				

Denotations: log. — logarithmic law; inv. log. — inversely logarithmic law; cu — cubic law; par. — parabolic law; paralin. — paralinear law; lin. — linear law; incr. — increased oxidation rate.

Phase diagram of the Ti-O₂ system



Influence of temperature on the Ti oxidation rate



THE END