

Solventi non-acquosi

Protici (e.g. HF, H₂SO₄, NH₃, MeOH)

I solventi protici generano protoni solvatati per auto-ionizzazione

Aprotici (e.g. DMSO, DMF, acetone, CH₂Cl₂, CHCl₃)



Apolari (CCl₄, C₆H₁₂,...) **Polari** (e.g. CH₂Cl₂, CHCl₃, CH₃NO₂)

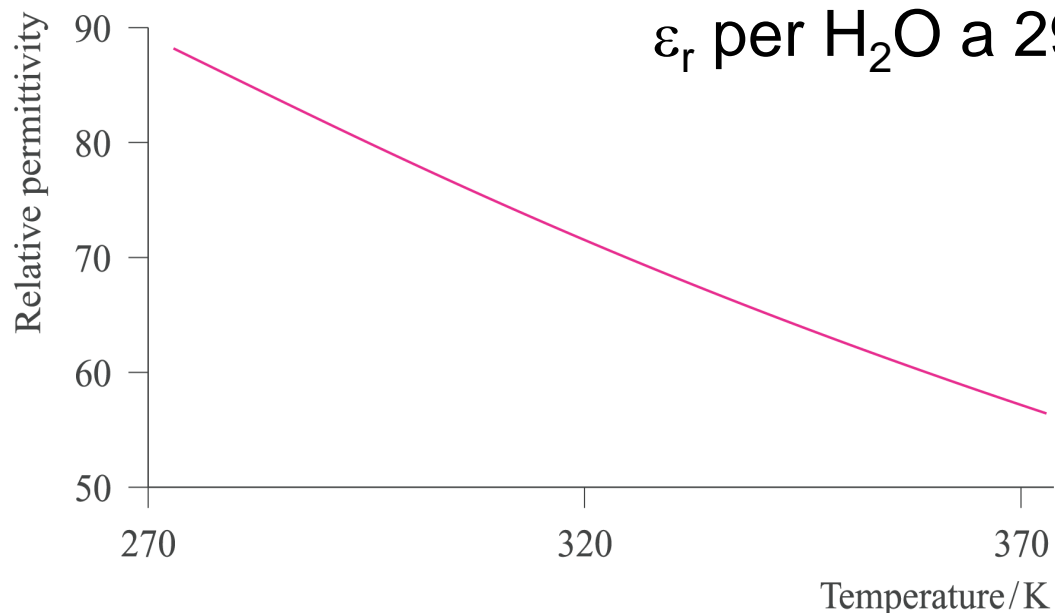
Costanti dielettriche (permittività)

$$E_c = \frac{e^2}{4\pi\epsilon_0 r} \quad \text{nel vuoto}$$

$$E_c = \frac{e^2}{4\pi\epsilon_r r} \quad \text{in un mezzo}$$

$$\epsilon_0 = 8.854 \times 10^{-12} \text{ F m}^{-1}$$

Costante dielettrica di H₂O



Costanti dielettriche (permittività)

$$E_c = \frac{e^2}{4\pi\epsilon_r r} \quad \text{in un mezzo}$$

Solvent	Formula [†]	Relative permittivity, ϵ_r	Dipole moment, μ / debye
Formamide	HC(O)NH ₂	109 (293 K)	3.73
Water	H ₂ O	78.7	1.85
Acetonitrile	MeCN	37.5 (293 K)	3.92
<i>N,N</i> -Dimethylformamide (DMF)	HC(O)NMe ₂	36.7	3.86
Nitromethane	MeNO ₂	35.9 (303 K)	3.46 ←
Methanol	MeOH	32.7	1.70
Ethanol	EtOH	24.3	1.69
Dichloromethane	CH ₂ Cl ₂	9.1 (293 K)	1.60
Tetrahydrofuran	C ₄ H ₈ O (structure 9.2)	7.6	1.75
Diethyl ether	Et ₂ O	4.3 (293 K)	1.15
Benzene	C ₆ H ₆	2.3	0

[†] Me = methyl; Et = ethyl.

DMSO

46.7

3.96

NH₃

25.0

1.47

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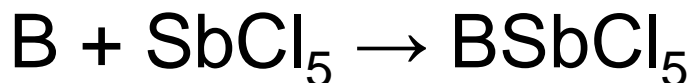
Aprotici (e.g. DMSO, DMF, acetone, CH₂Cl₂, CHCl₃)

Apolari (CCl₄, C₆H₁₂,...) **Polari** (e.g. CH₂Cl₂, CHCl₃, CH₃NO₂)

Coordinanti (e.g. DMSO, CH₃CN)

Donation Number (DN)

per valutare se (e quanto) un solvente è coordinante



$$\text{DN} \equiv -\Delta H$$

	DN	ϵ_r
DMSO	29.8	46.7
CH ₃ NO ₂	2.7	38.6
py	33.1	12.3
etere etilico	19.2	4.3

non c'è correlazione fra DN e costante dielettrica

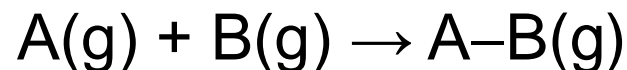
Table 4.4 Drago–Wayland parameters for some acids and bases*

	<i>E</i>	<i>C</i>
<i>Acids</i>		
Antimony pentachloride	15.1	10.5
Boron trifluoride	20.2	3.31
Iodine	2.05	2.05
Iodine monochloride	10.4	1.70
Phenol	8.86	0.90
Sulfur dioxide	1.88	1.65
Trichloromethane	6.18	0.32
Trimethylboron	12.6	3.48
<i>Bases</i>		
Acetone	2.02	4.67
Ammonia	2.78	7.08
Benzene	0.57	1.21
Dimethylsulfide	0.70	15.26
Dimethylsulfoxide	2.76	5.83
Methylamine	2.66	12.00
<i>p</i> -Dioxane	2.23	4.87
Pyridine	2.39	13.10
Trimethylphosphine	17.2	13.40

* *E* and *C* parameters are often reported to give ΔH in kcal mol⁻¹; we have multiplied both by $\sqrt{(4.184)}$ to obtain ΔH in kJ mol⁻¹.

Parametri di Drago – Wayland

ogni specie è caratterizzata da due parametri *E* e *C*

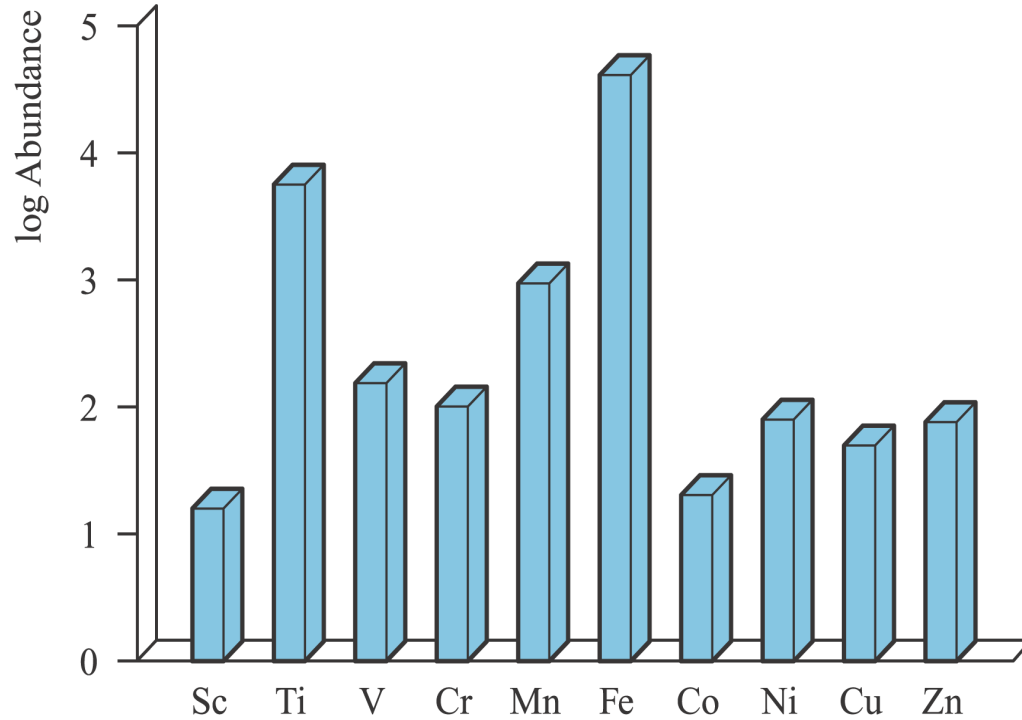


$$-\Delta H^\circ (A-B) = E_A E_B + C_A C_B$$



Entalpia standard di formazione

Abbondanze relative nella crosta terrestre



Metallurgia estrattiva

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graph TD; A([Metallurgia estrattiva]) --> B([Processi idrometallurgici]); A --> C([Processi pirometallurgici]);
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Processi idrometallurgici

Processi pirometallurgici

Processi pirometallurgici

Minerale grezzo

Arrostimento

Ossido

Riduzione chimica (*smelting*) o
elettrolitica (*electrowinning*)

Metallo

Processi idrometallurgici

Minerale grezzo

Lisciviazione

Ione o complesso del metallo

Riduzione

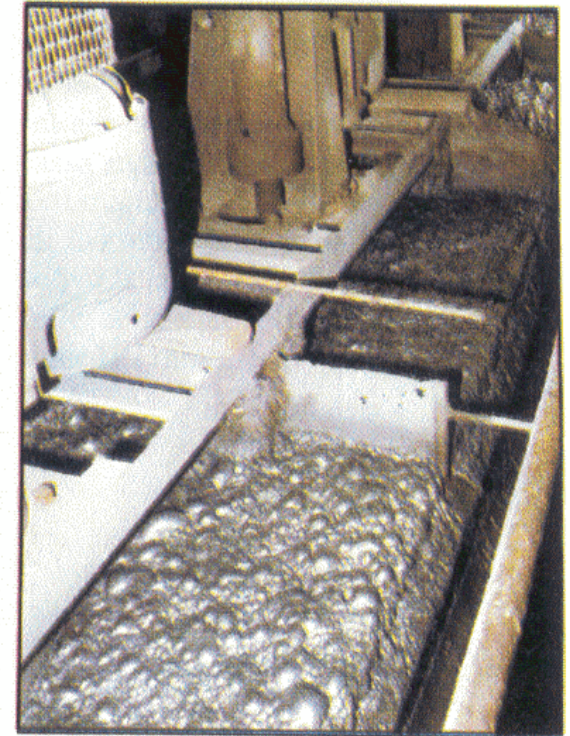
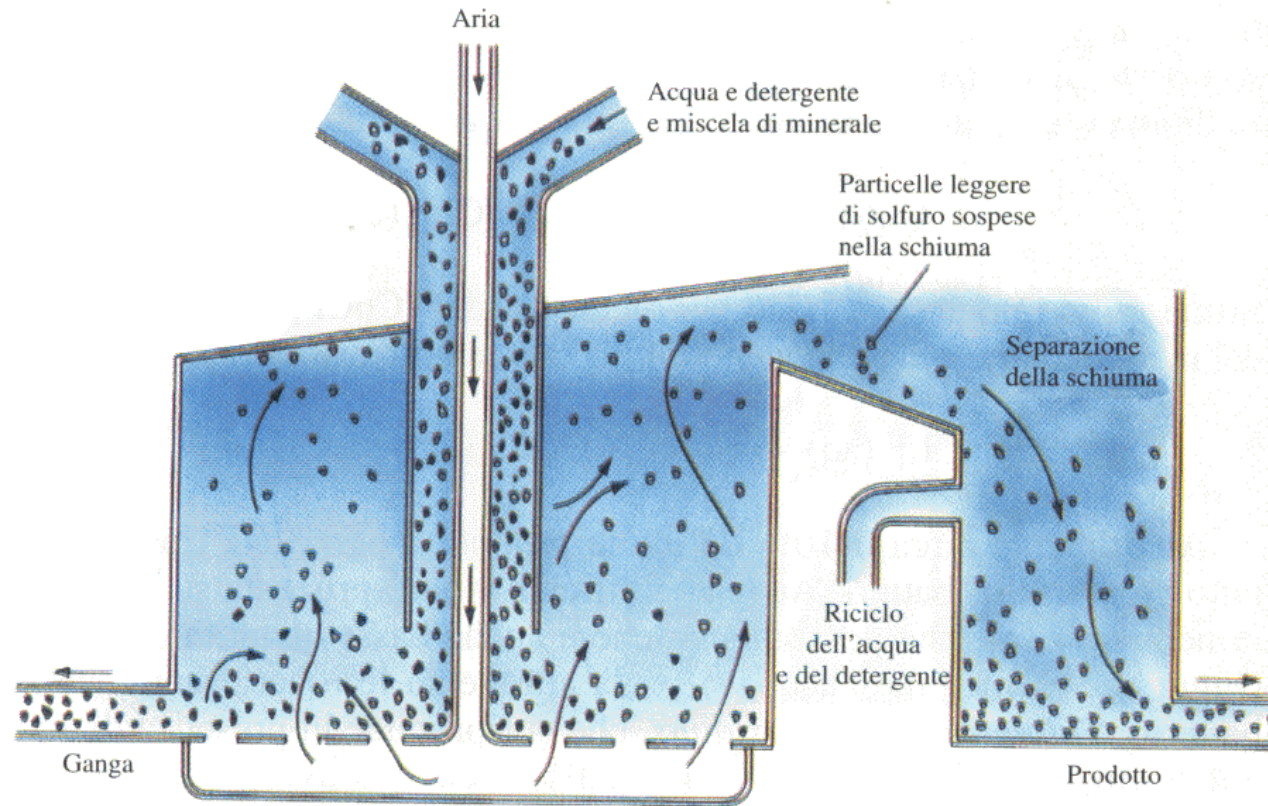
Metallo

Miniera a cielo aperto di calcopirite, CuFeS_2 di El Chino nel Nuovo Messico





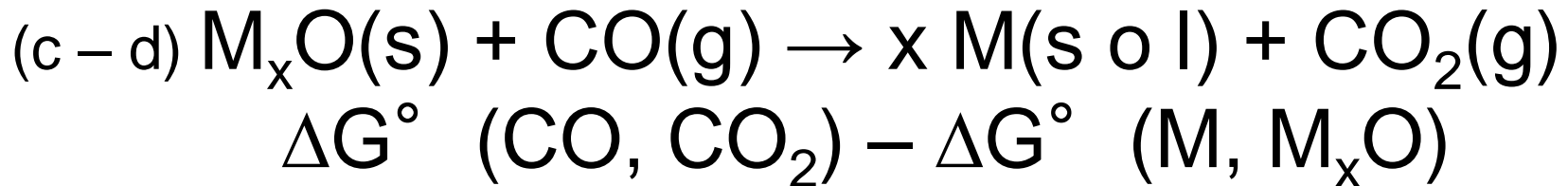
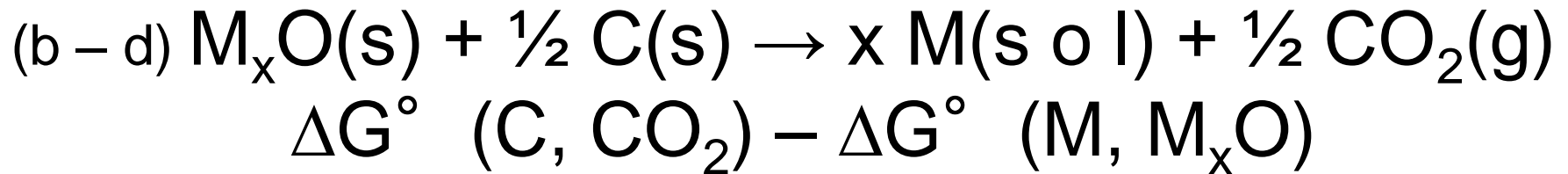
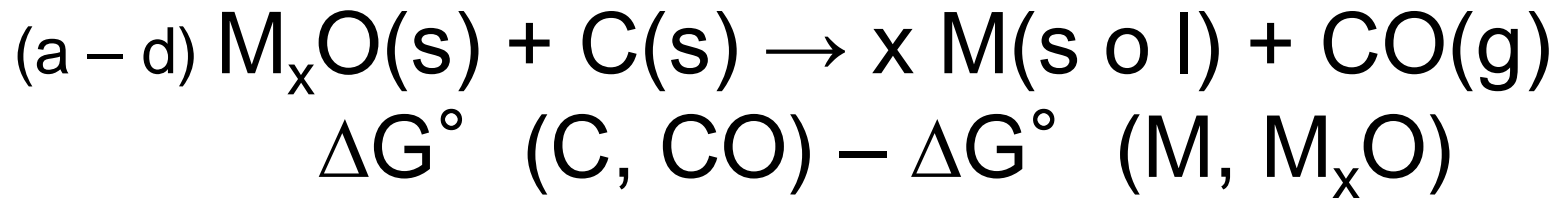
Flottazione di calcopirite CuFeS_2



Cu%: da 0.8–1% → 15–30%

Aspetti termodinamici dei processi di riduzione con carbone o CO

- a) $\text{C(s)} + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{CO(g)}$ ΔG° (C,CO)
- b) $\frac{1}{2}\text{C(s)} + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \frac{1}{2}\text{CO}_2(\text{g})$ ΔG° (C,CO₂)
- c) $\text{CO(g)} + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})$ ΔG° (CO,CO₂)
- d) $x \text{M(s o l)} + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{M}_x\text{O(s)}$ ΔG° (M,M_xO)



una di queste reazioni complessive deve avere ΔG° negativo

Diagramma di Ellingham

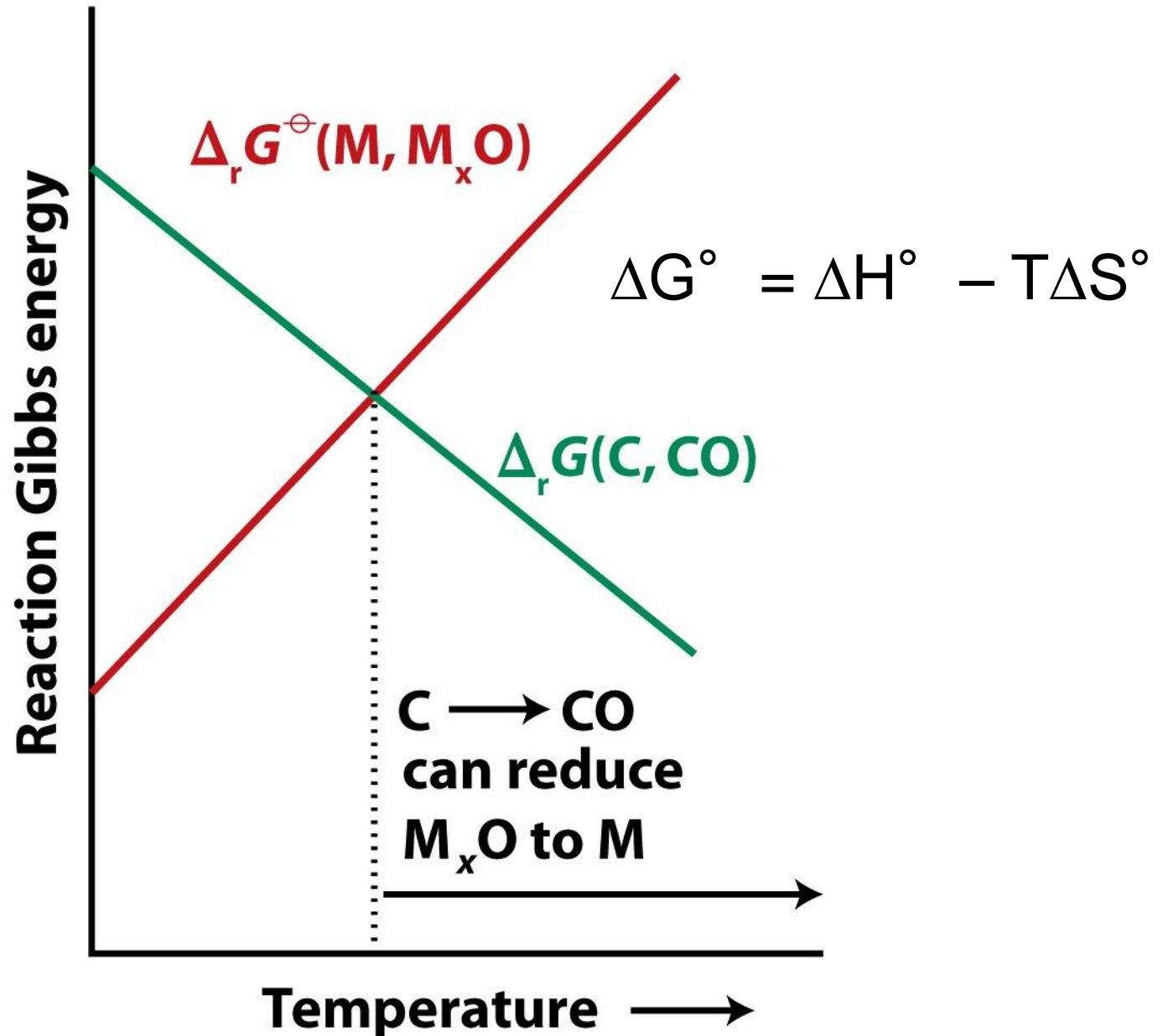
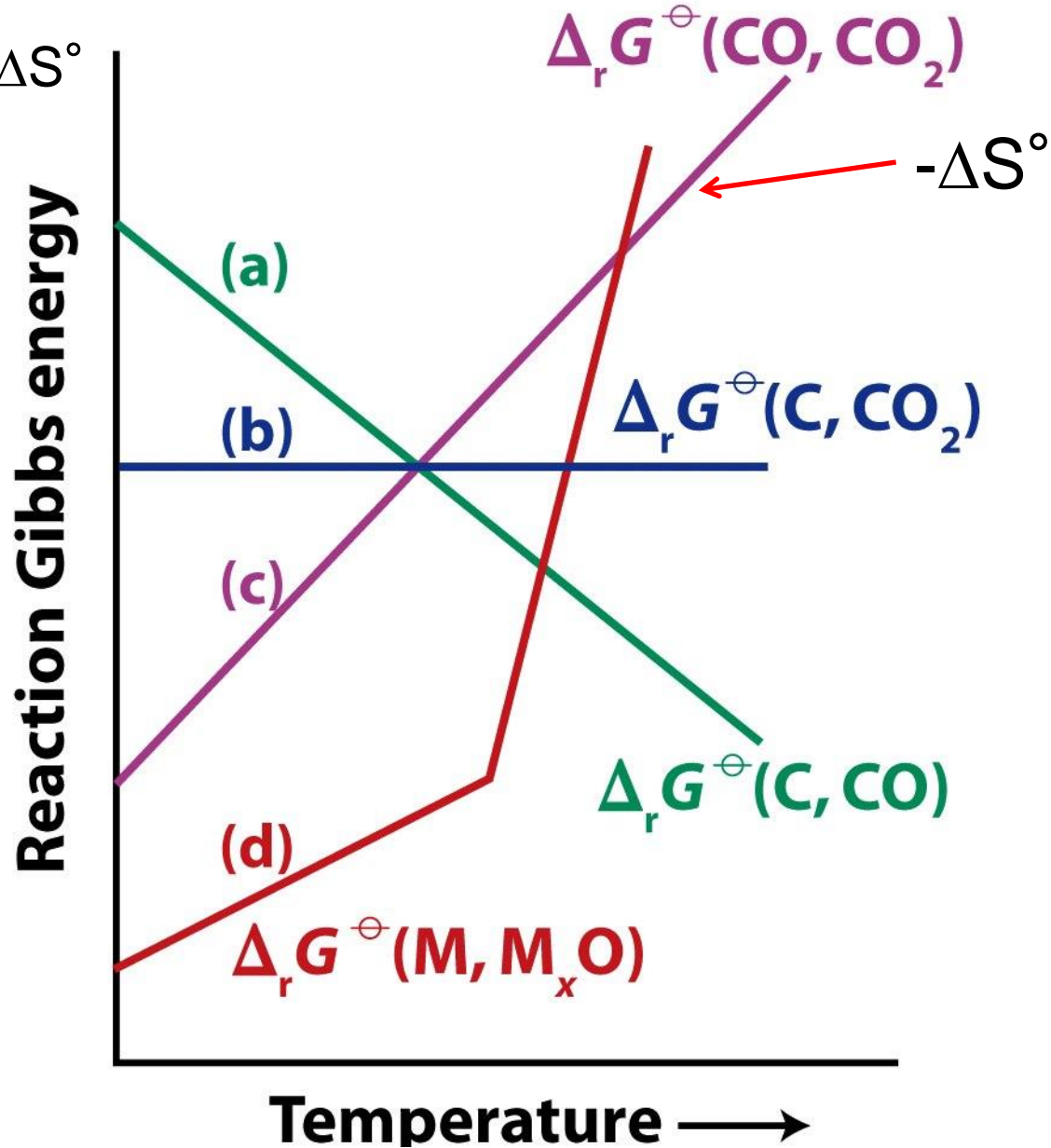
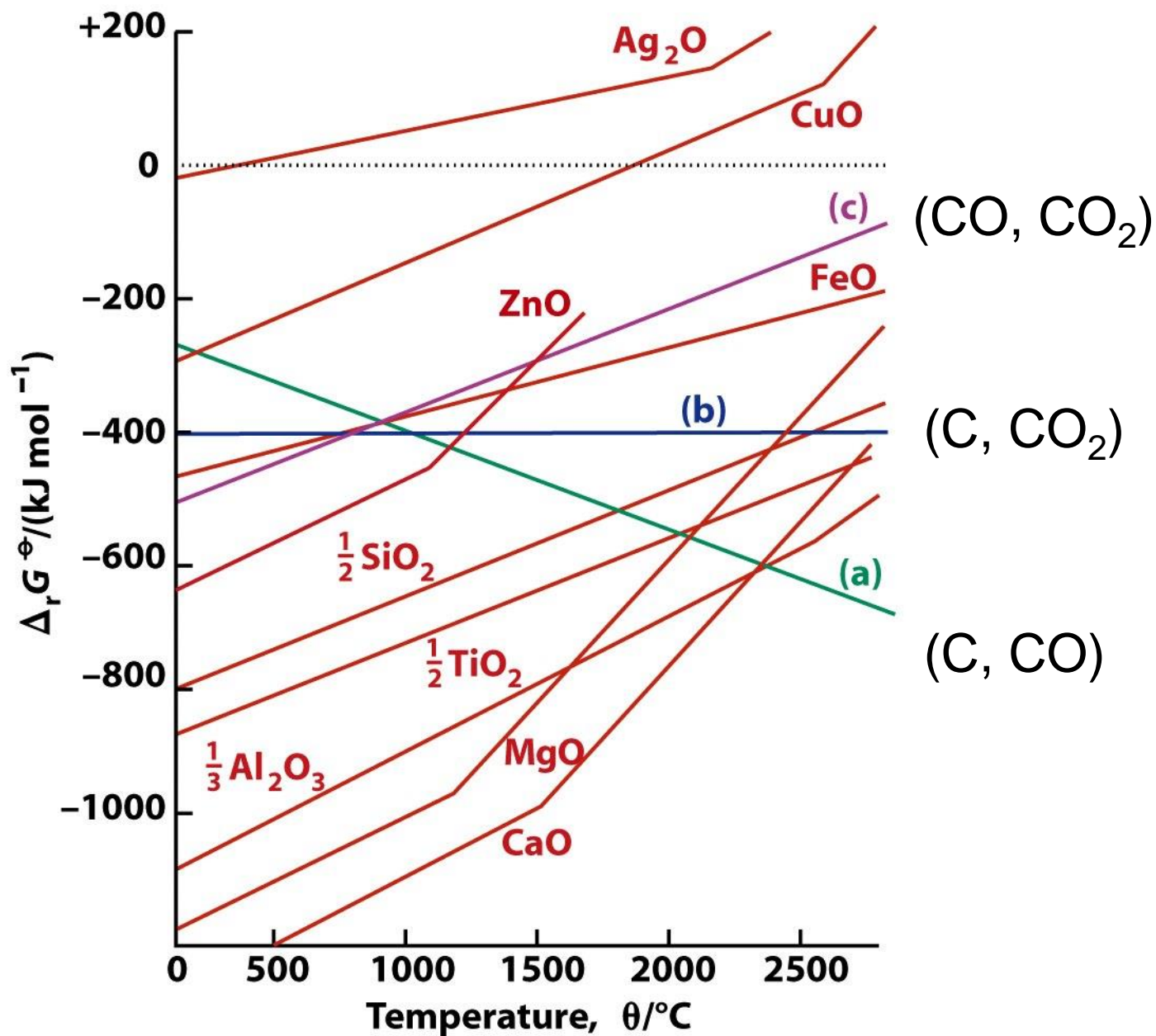
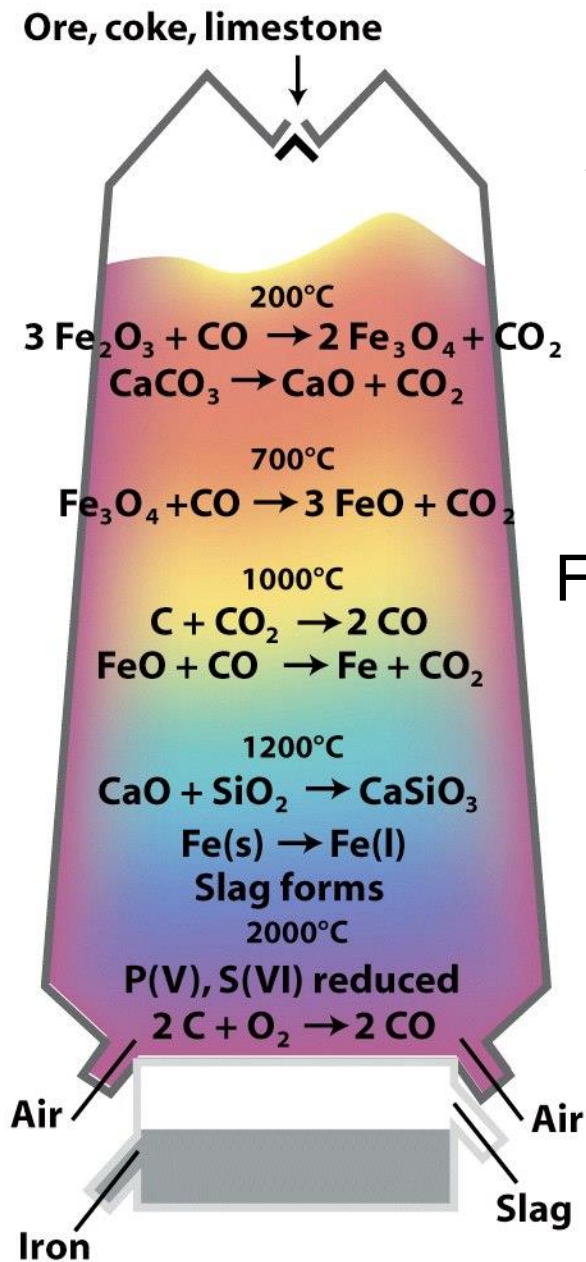


Diagramma di Ellingham

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

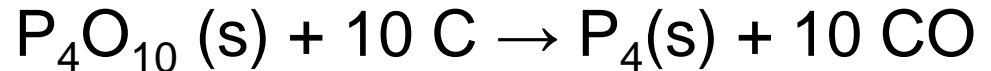
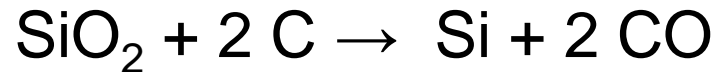
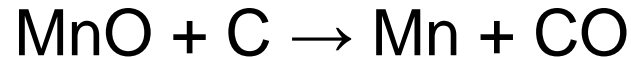
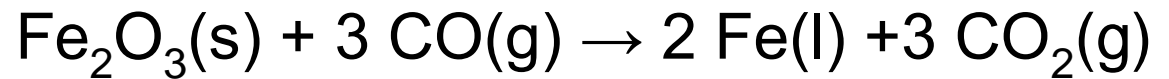




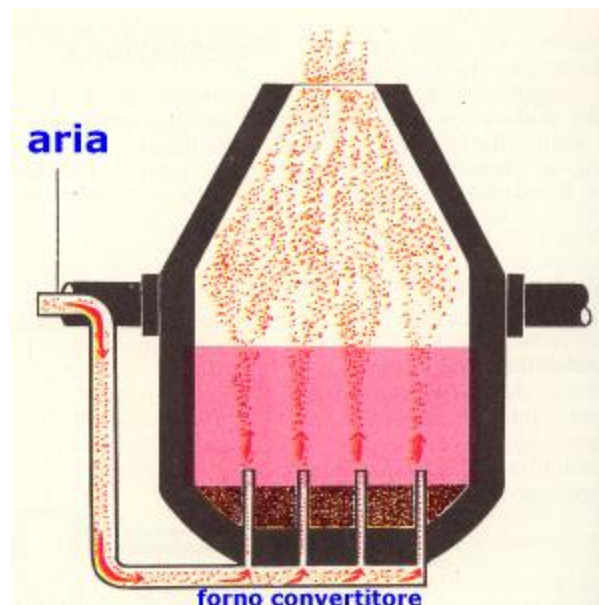
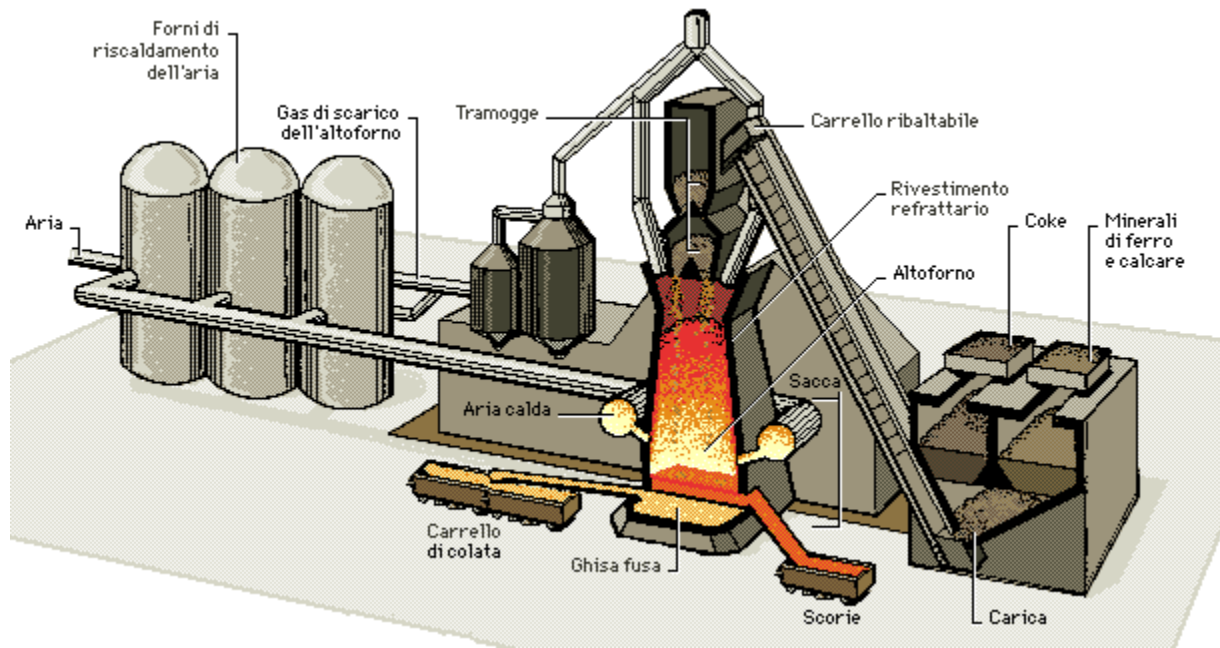


Altoforno

1 t di ghisa richiede ca.:
 1.7 t di minerale di ferro,
 0.5 t di coke,
 0.25 t di calcare.



Ghisa grezza: 4.5% C; 1.7% Mn; 0.3% P; 0.04% S; 1% Si



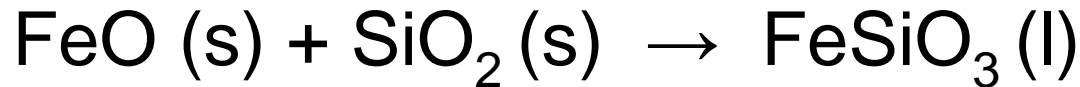
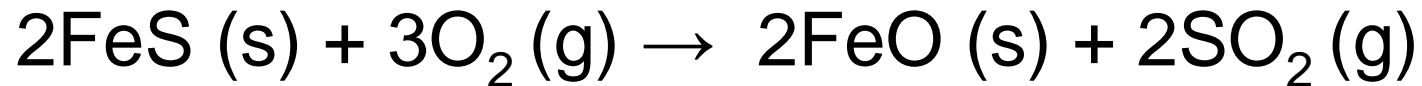
Decarburazione
della ghisa

Processo pirometallurgico della calcopirite

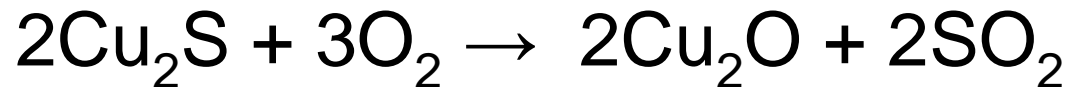


1. Arrostitimento in forno a riverbero per eliminare Fe

1400 C



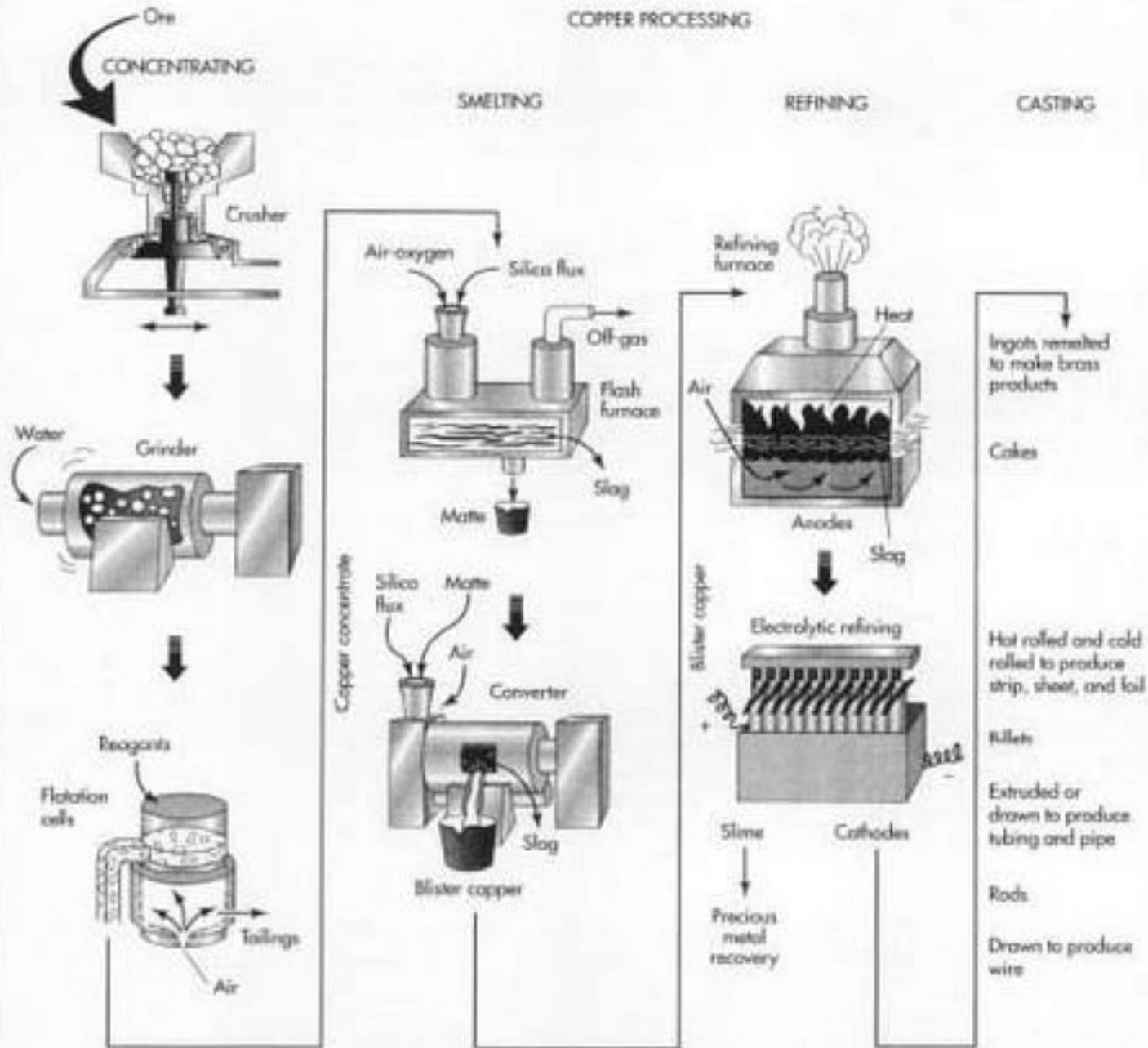
2. Smelting della metallina di rame in convertitori



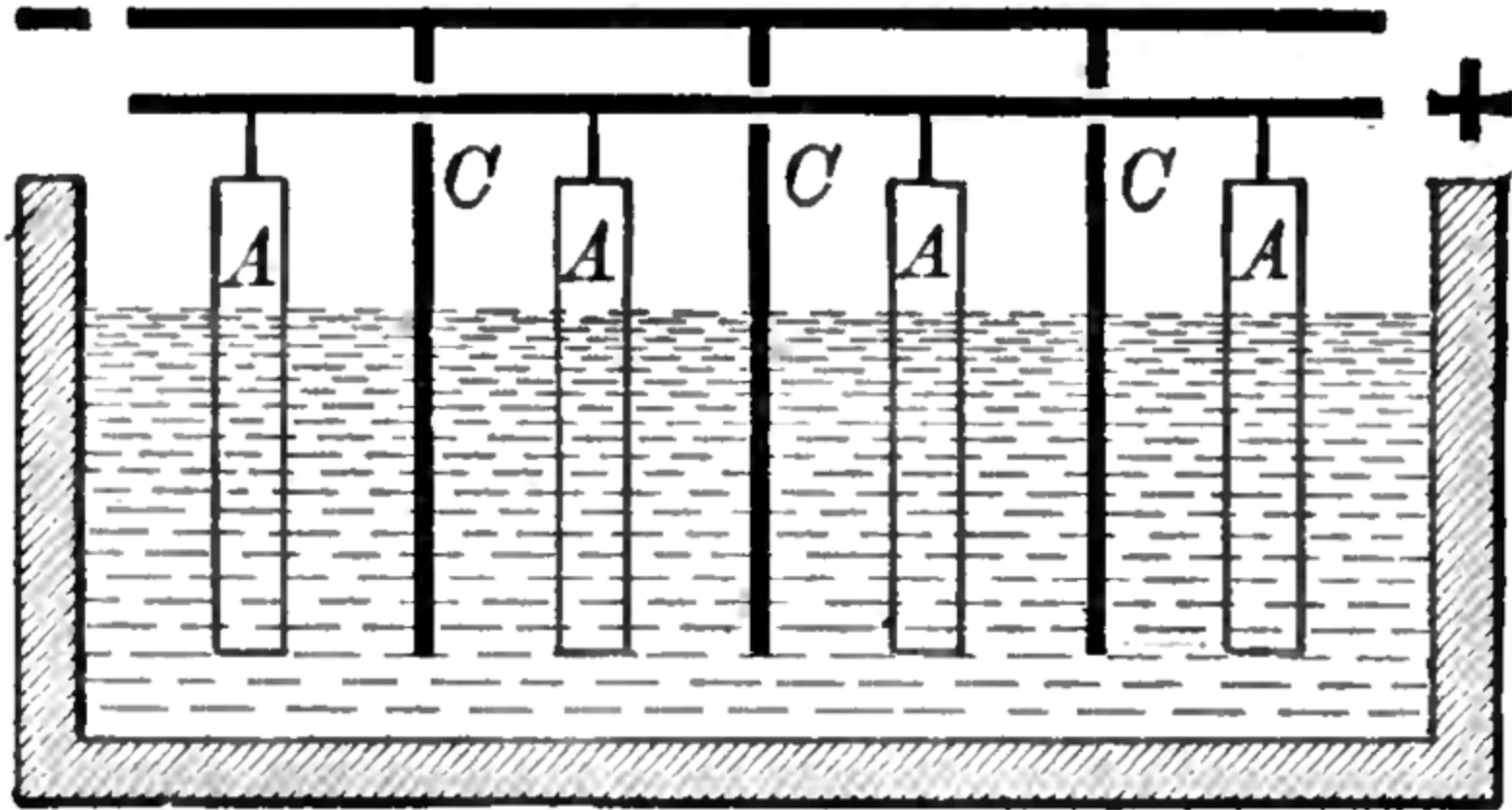
Blister di rame

Per 1 t di Cu grezzo: 1.5 t FeSiO_3 (scoria) + 2 t SO_2

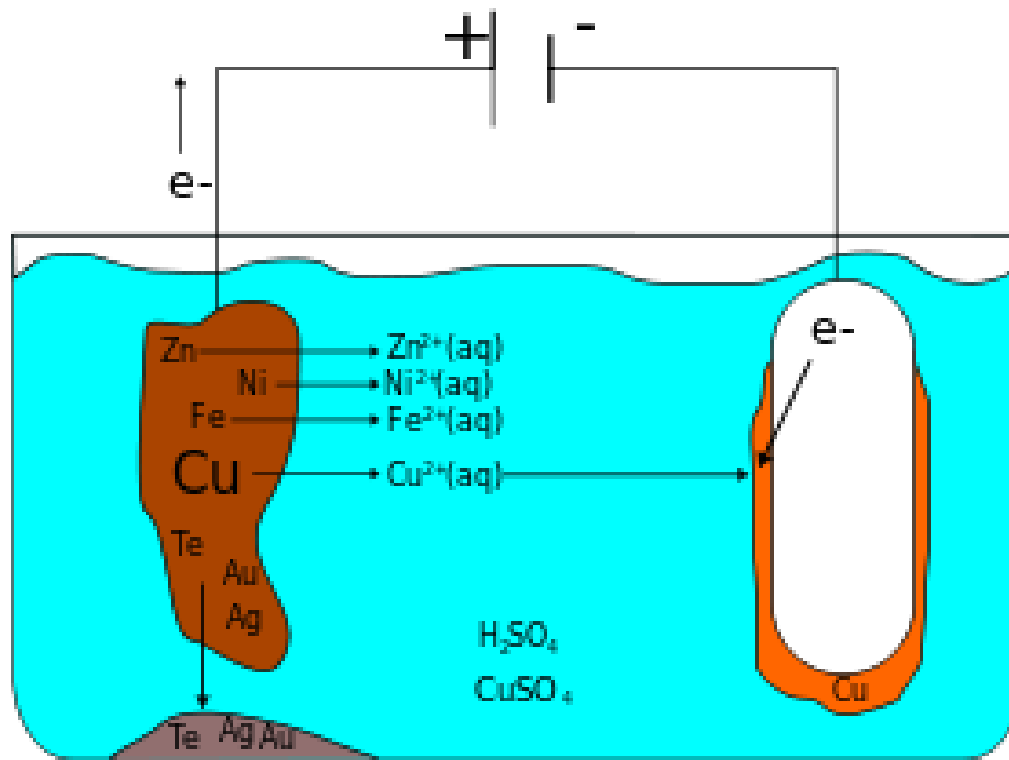
COPPER PROCESSING



Raffinazione elettrolitica del rame



0.2–0.3 V, 10.000 – 20.000 A



Fanghi anodici

Processo idrometallurgico per l'estrazione dell'oro

