



*Química Analítica II:
Separación de Ni (II) y
Cd(II) a pH impuesto*

Estudio gráfico.

*Dr. Alejandro Baeza
Fac. Química. UNAM*



¿Porqué separar Ni(II) y Cd(II)?:



Nano, coche del futuro:

La electricidad se almacena en 19 baterías de níquel-cadmio cuya vida estimada es de 10 años, su recarga se puede realizar directamente desde una toma de corriente doméstica de 220V, necesita de 8 horas para tener una recarga completa y 5 horas para recargar el 80%. Puede conseguir una velocidad máxima de 100 km/h, llega a 50 km/h en 7 segundos y supera pendientes del 30% (un Pontiac Matiz de 65 HP sube pendientes de 40%) lo que lo limita para su uso exclusivo en ciudad.



Water Air Soil Pollut

DOI 10.1007/s11270-008-9697-9

Electrochemical Recovery of Cadmium from Simulated Waste Nickel–Cadmium Battery Solutions



R. Mayén-Mondragón • J. G. Ibanez •
R. C. Vasquez • A. Baeza • M. T. Oropeza

Received: 17 October 2007 / Accepted: 24 March 2008

© Springer Science + Business Media B.V. 2008

Abstract The selective recovery of Cd from simulated spent nickel–cadmium battery solutions was achieved

Keywords Cadmium recovery • Electrochemical recovery • Hazardous waste • Metal recovery • Nickel recovery

and sulfuric acids. The latter was selected for further study of the recovery step. Nitrate media were found to be unsuitable for Cd recovery since nitrates are reduced at the required deposition potentials. Cd(II) deposition on Cd electrodes is favored in sulfate or chloride media since it occurs at a potential some 200 mV less negative than that of Ni(II). A good percent Cd recovery (>90%) with high selectivity (approximately 0% Ni) and a reasonably high current efficiency (>80%) can be achieved under appropriate conditions. The irreversible nature of Ni(II) reduction provides the necessary framework to achieve such a selective separation.

R. Mayén-Mondragón · J. G. Ibanez (✉) · R. C. Vasquez
Department of Chemical Engineering and Sciences,
Universidad Iberoamericana,
Prol. Reforma #880,
01219 Mexico, Mexico
e-mail: jorge.ibanez@uia.mx

A. Baeza
Facultad de Química,
Universidad Nacional Autónoma de México,
Circuito Exterior, Ciudad Universitaria,
04510 Mexico, Mexico

M. T. Oropeza
Instituto Tecnológico de Tijuana,
Calz. del Tecnológico s/n, Fracc. Tomas Aquino,
22370 Tijuana, Mexico

1 Introduction

Spent nickel–cadmium (NiCad) batteries still represent an important pollution problem. In fact, the US, Japan and some European countries have established tight regulations for their disposal, mainly due to the high toxicity of cadmium. Nickel compounds possess different degrees of toxicity, but that of cadmium compounds is typically more acute and bioaccumulation may represent important threats (Topperwien et al. 2007). Even though NiCad's tend to be phased out in some developed countries, they still cover a large portion of the market for emergency lights, alarms, portable electric tools, and other home and portable devices that require rechargeable batteries (Fujimoto 1997). In Canada alone, the annual shipments of NiCad consumer battery units were 9.1×10^6 in 2000, and the projection is 22.4×10^6 for 2010 (Environment Canada 2007). Such an increase is most likely due to their lower cost as compared to that of the alternative Li-ion and Ni-hydride batteries (Lam et al. 2007).

Sales of sealed NiCad batteries in the US, Japan and Europe totaled nearly 10^9 units in 1998 (Hake 1998); in spite of the lack of precise data, it can be anticipated that very few of them have been recycled. For example, only 1% of the consumer secondary

Federal Department of the Environment, Environment Canada 2007). A key consideration is that improperly disposed batteries may be mixed up with waste that ends up in municipal incinerators, where cadmium readily volatilizes (b.p. 767°C) (Rajeshwar and Ibanez 1997). In addition, those that remain in open landfills may undergo lixiviation as a result of acid deposition; such lixiviates may enter groundwater streams and create a potential danger to nearby users.

Recycling processes applicable to this case can be grouped into hydrometallurgical and pyrometallurgical (Van Deelen 1989). The first group normally entails several separation stages including acid dissolution, solvent extraction, and pH-precipitation. In the second group, high temperatures are utilized to volatilize the main components. Some technological processes involve the combination of both types of recovery schemes. Other approaches are based on physicochemical adsorption and solvent extraction (Lam et al. 2007; Srivastava et al. 2006).

Alternatively, electrochemical techniques offer the possibility of achieving the selective separation and recovery in two steps. This selectivity depends on the composition of the solution containing the desired metals, since phenomena like complex formation and standard potential modification may play a key role in their recuperation. For example, in the electrochemical recovery of Cd from the anodes in spent NiCd batteries

NiCd's include HNO_3 , HCl and H_2SO_4 . Since acids are known to influence the metal deposition potential, their effect was also analyzed. The acidic medium yielded the best results with constant potential electrolysis in this screening stage (i.e., a sulfate medium was then selected for further study. Since the electrochemical behavior during Cd deposition is different with various electrodes (Rozik and Trnkova 2006), we selected Cd metal as the substrate in order to promote surface recognition by the depositing ions, and analyzed the effect of mass transfer with a rotating disk electrode. The targeted selective Cd recovery was achieved in a simple system (i.e., without an exchange membrane) as discussed below.

2 Experimental Details

Constant potential electrolyses were used for deposition experiments and linear potential sweep process characterization. For both techniques, a C-100 W Voltammetric Analyzer (Bioanalytical Systems) was employed. A controlled growth mercury drop electrode (CGME, BAS) was used for the polarographic analysis. An analytical rotator (AF-ASR, Pine Instruments) was used for the convection experiments. An Ag/AgCl electrode (BAS) was the reference electrode. Potentials in this work are referred to it, and a normal

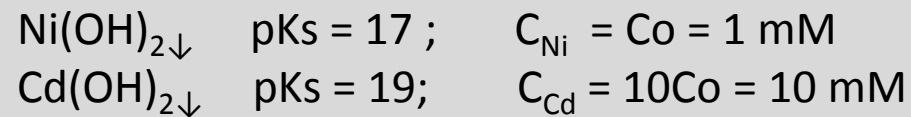
Separación de Ni(II) y Cd(II) decimolares por precipitación *iónica**, a pH impuesto:

Para ambos cationes:



* *No es necesario considerar a las especies moleculares o metalatos, i.e., $\alpha_{\text{M(OH)}} = 1$.*

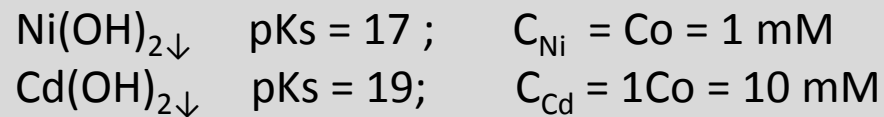
Separación de Ni(II) y Cd(II) decimolares por precipitación *iónica**, a pH impuesto:



Para ambos cationes:

$$K_s = [M^{2+}][OH^-]^2$$

Separación de Ni(II) y Cd(II) decimolares por precipitación *iónica**, a pH impuesto:



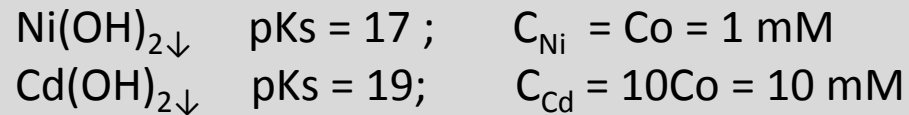
Para ambos cationes:

A partir del K_w :

$$K_w = [\text{H}^+][\text{OH}^-]$$

$$[\text{OH}^-] = K_w / [\text{H}^+]$$

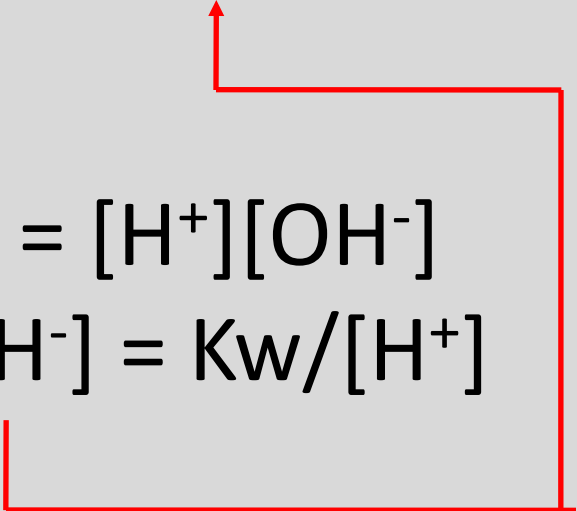
Separación de Ni(II) y Cd(II) decimolares por precipitación *iónica**, a pH impuesto:



Para ambos cationes:

$$K_s = [\text{M}^{2+}][\text{OH}^-]^2$$

A partir del $K_w = [\text{H}^+][\text{OH}^-]$

$$[\text{OH}^-] = K_w / [\text{H}^+]$$


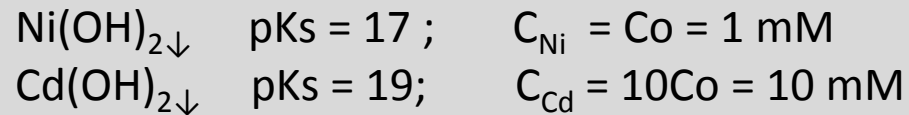
Separación de Ni(II) y Cd(II) decimolares por precipitación *iónica**, a pH impuesto:



Para ambos cationes el Ks de los hidróxidos en función del pH:

$$K_s = [M^{2+}](K_w/[H^+])^2$$

Separación de Ni(II) y Cd(II) decimolares por precipitación *iónica**, a pH impuesto:



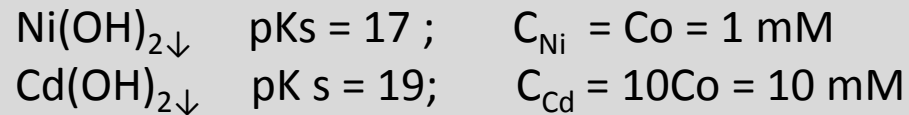
Para ambos cationes el Ks de los hidróxidos en función del pH:

$$K_s = [M^{2+}](K_w/[H^+])^2$$

Ya que $K_w = 10^{-pK_w}$ y $[H^+] = 10^{-pH}$

Para $[M^{2+}] = S$ (*concentración metal soluble*) :

Separación de Ni(II) y Cd(II) decimolares por precipitación *iónica**, a pH impuesto:



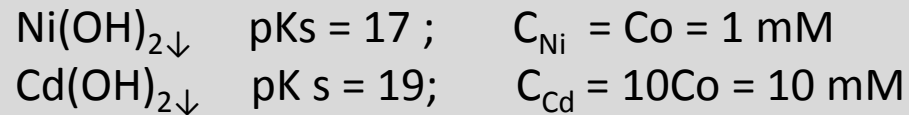
Para ambos cationes el Ks de los hidróxidos en función del pH:

$$K_s = [M^{2+}](K_w/[H^+])^2$$



$$K_s = (S) (10^{-2\text{pKw}+2\text{pH}})$$

Separación de Ni(II) y Cd(II) decimolares por precipitación *iónica**, a pH impuesto:



Para ambos cationes el Ks de los hidróxidos en función del pH:

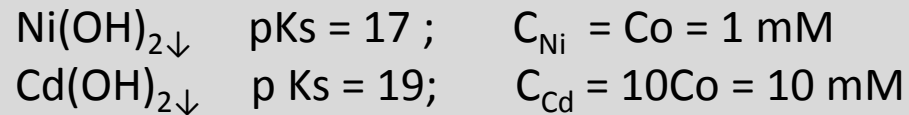
$$K_s = [M^{2+}](K_w/[H^+])^2$$



$$K_s = (S) (10^{-2pK_w+2pH})$$

Linearizando logarítmicamente:

Separación de Ni(II) y Cd(II) decimolares por precipitación *iónica**, a pH impuesto:



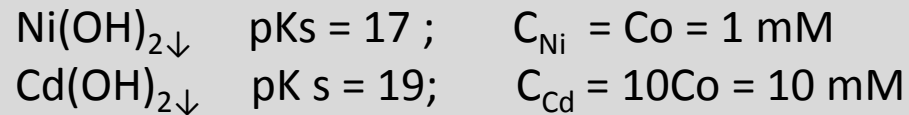
Para ambos cationes el Ks de los hidróxidos en función del pH:

Linearizando logarítmicamente:

$$K_s = (S) (10^{-2pK_w + 2pH})$$

$$\log S = -pK_s + 2pK_w - 2pH$$

Separación de Ni(II) y Cd(II) decimolares por precipitación *iónica**, a pH impuesto:



Para ambos cationes el K_s de los hidróxidos en función del pH:

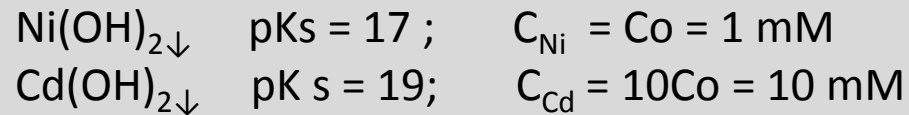
Linearizando logarítmicamente:

$$K_s = (S) (10^{-2pK_w + 2pH})$$

$$\log S = -pK_s + 2pK_w - 2pH$$

$$\log S = -pK_s + 28 - 2pH$$

Separación de Ni(II) y Cd(II) decimolares por precipitación *iónica**, a pH impuesto:



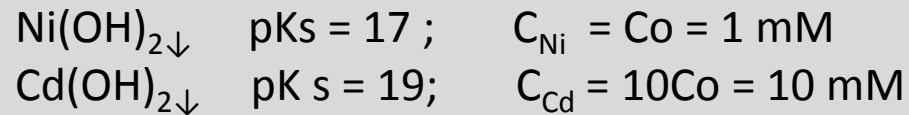
Para el Níquel:

$$\log S = -pKs + 28 - 2pH$$

$$\log S = -17 + 28 - 2pH$$

$$\log S = 11 - 2pH$$

Separación de Ni(II) y Cd(II) decimolares por precipitación *iónica**, a pH impuesto:



Para el Cadmio:

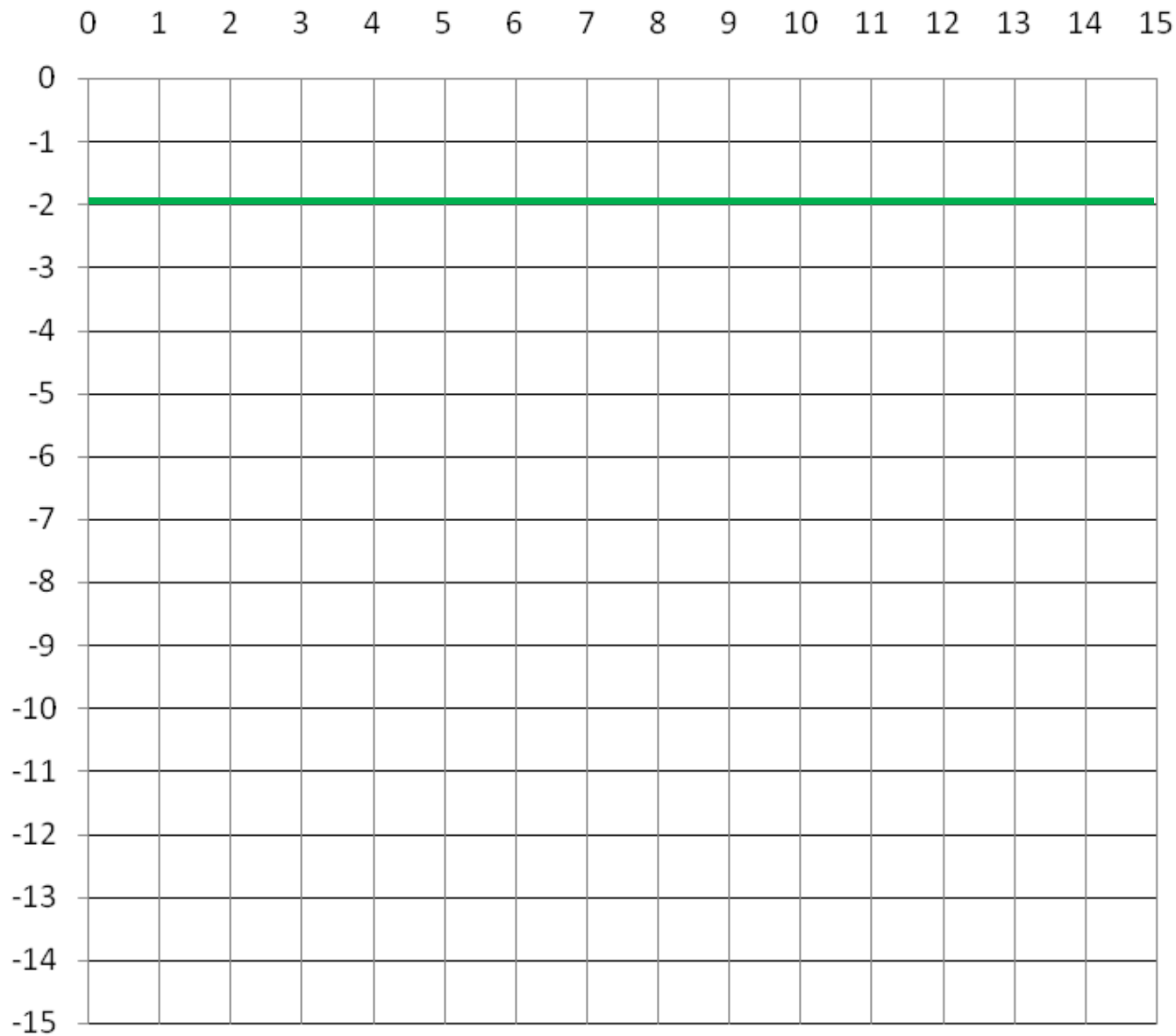
$$\log S = -\text{pKs} + 28 - 2\text{pH}$$

$$\log S = -19 + 28 - 2\text{pH}$$

$$\log S = 9 - 2\text{pH}$$

pH

Para el Cadmio:
 $\log C_M = -2$

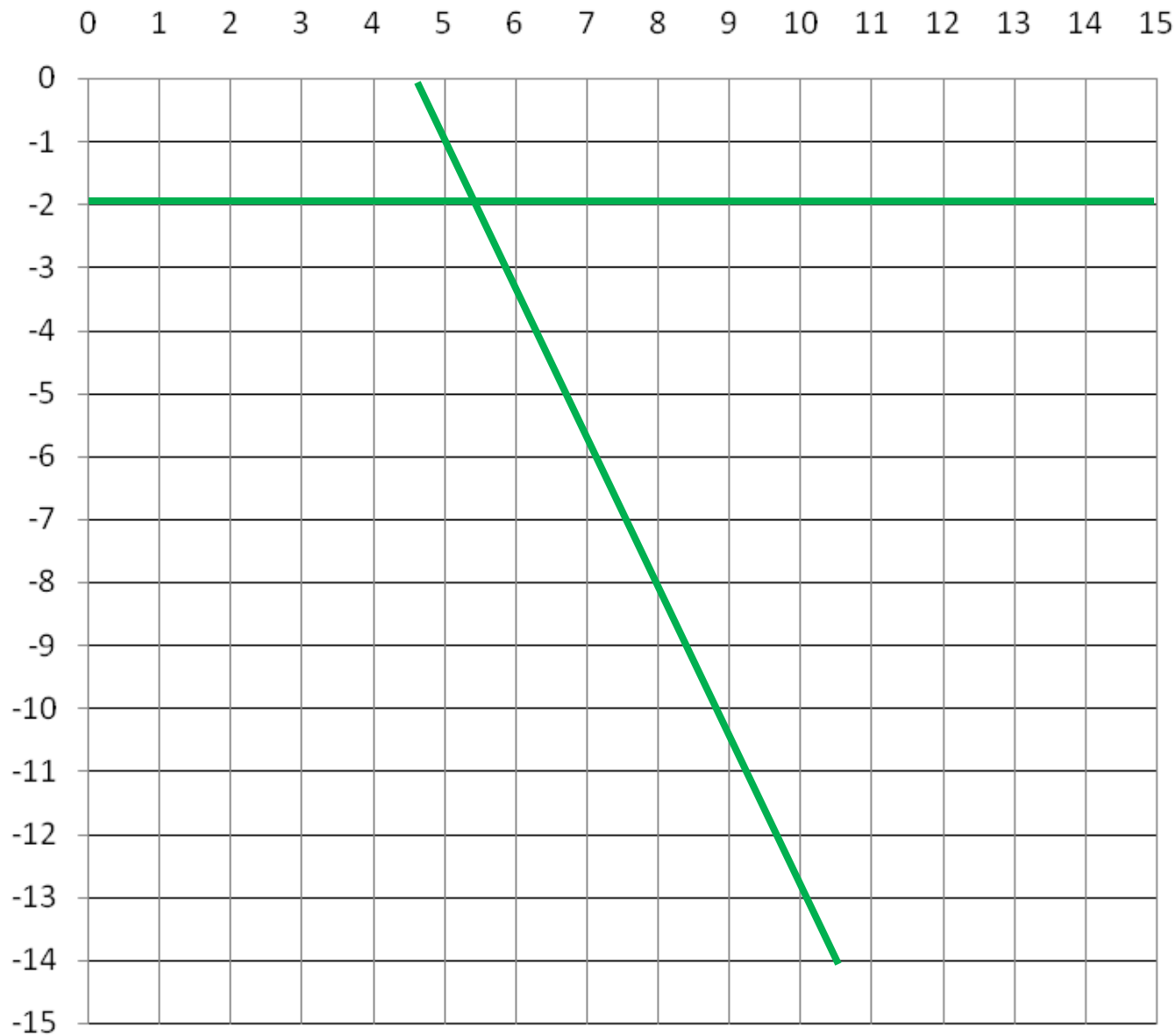


log S'

pH

Para el Cadmio:
 $\log C_M = -2$

$\log S = 9 - 2pH$

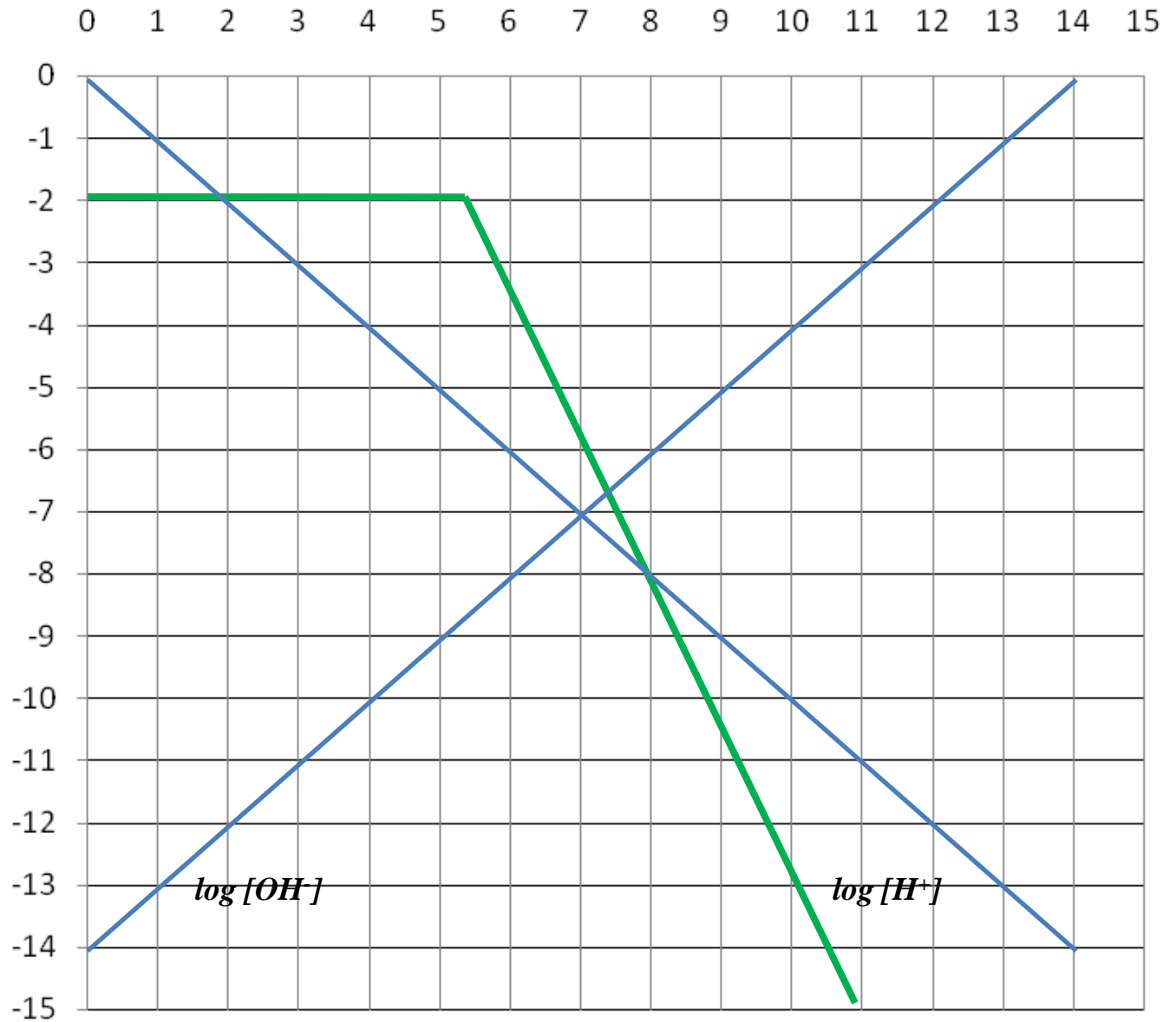


log S'

pH

Para el Cadmio:
 $\log C_M = -2$

$\log S = 9 - 2pH$

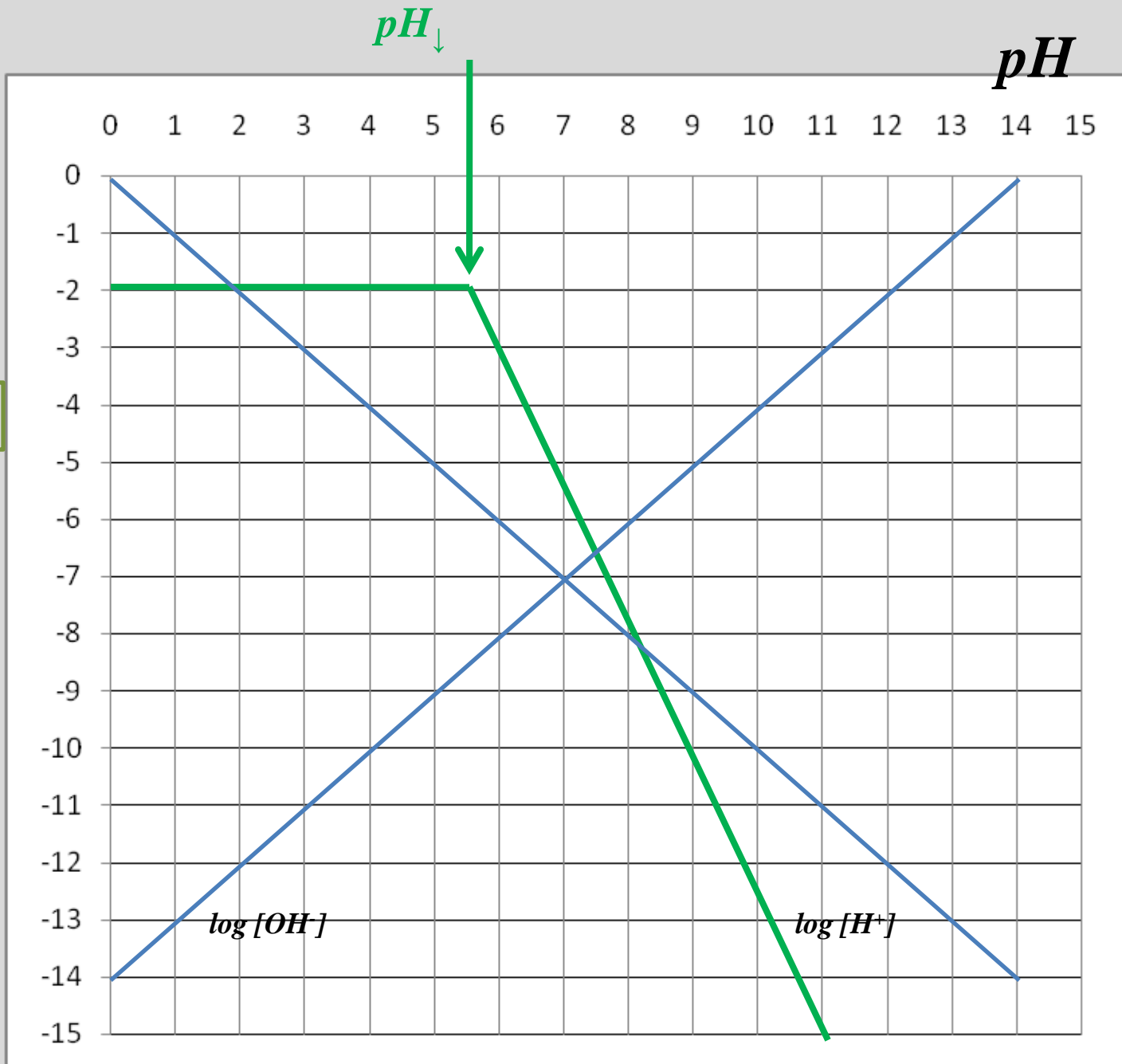


$\log S'$

Para el Cadmio:
 $\log C_M = -2$

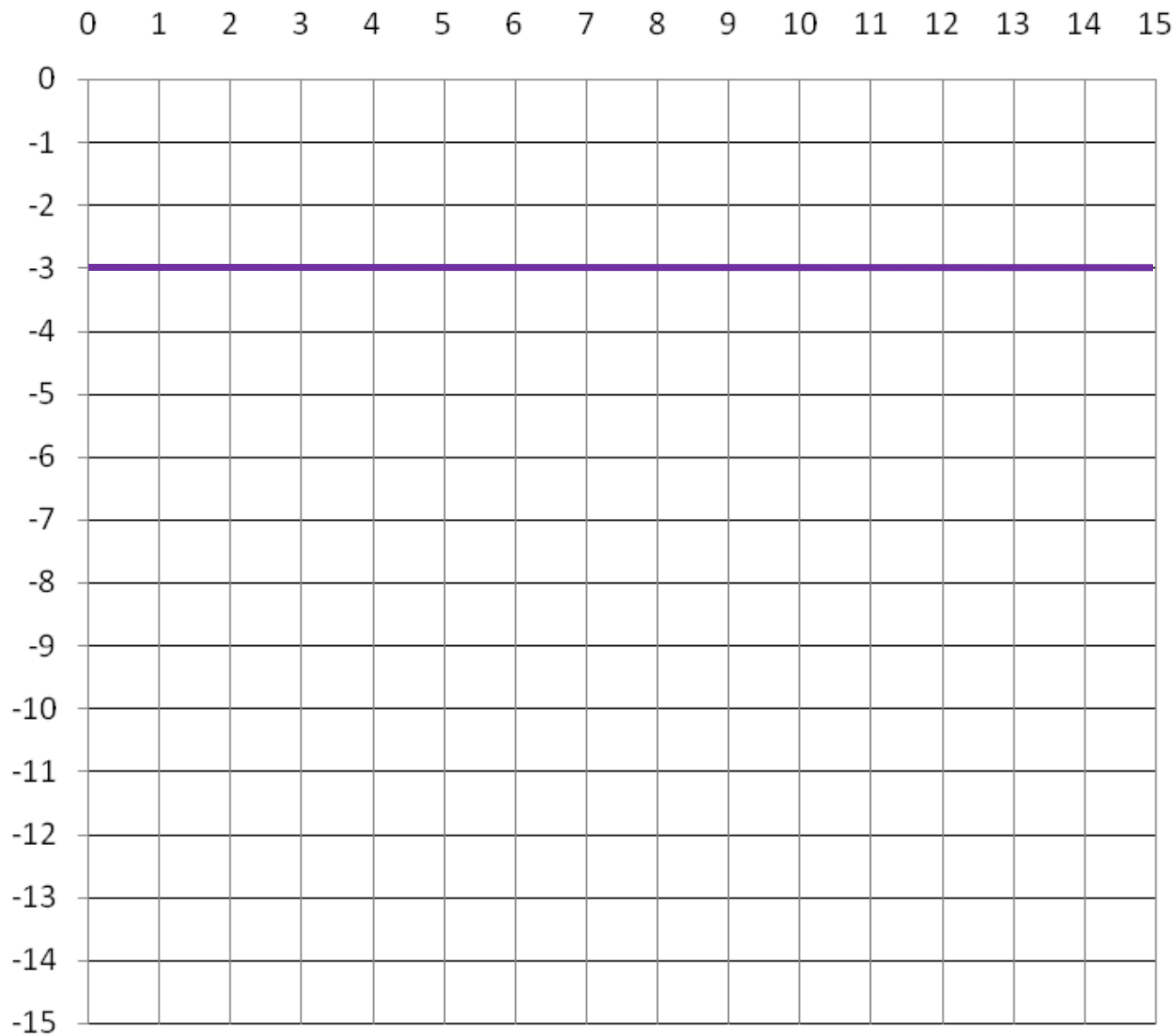
$$\log S = 9 - 2pH$$

$\log S'$



pH

Para el Níquel:
 $\log C_M = -3$

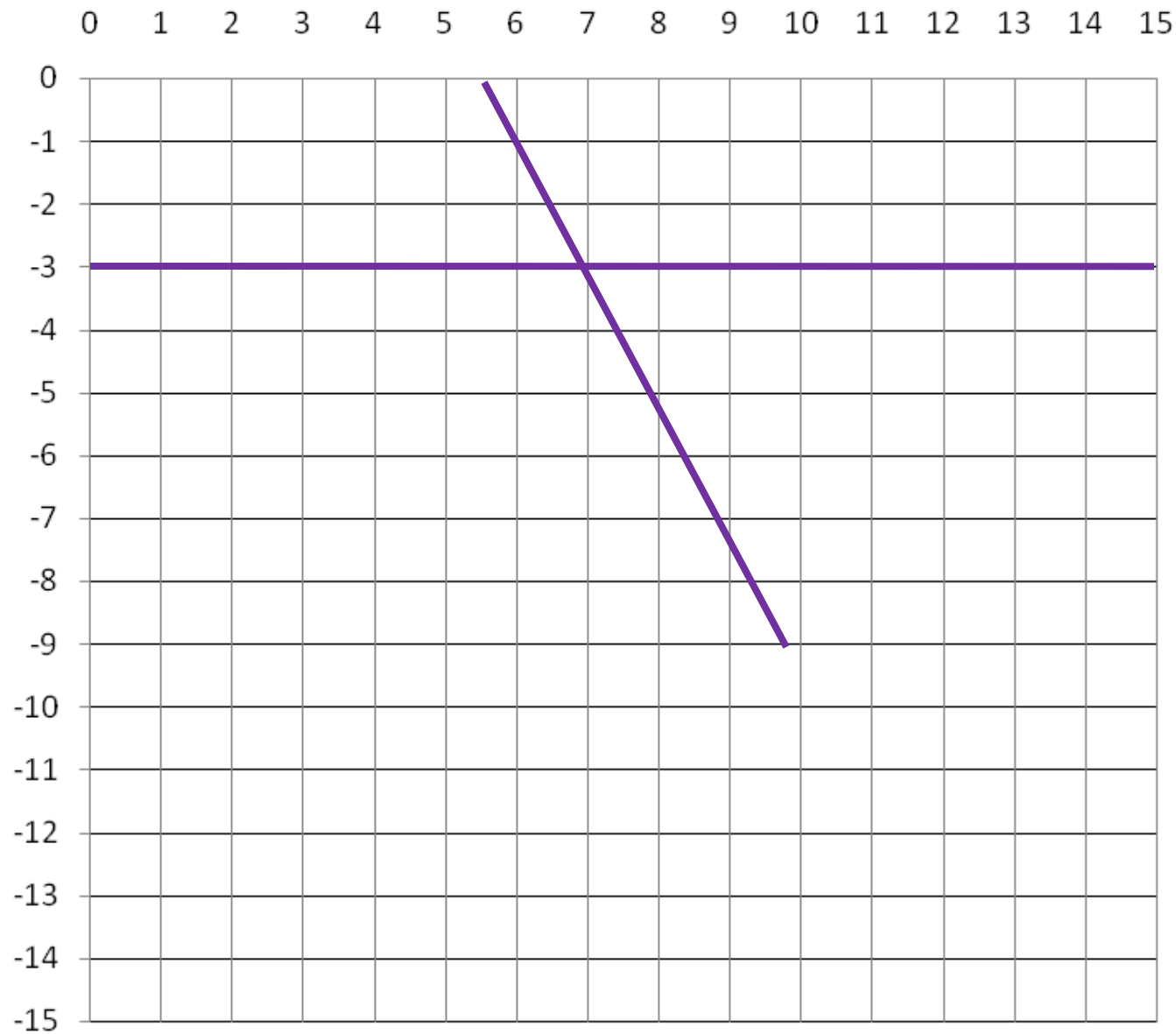


log S'

pH

Para el Níquel:
 $\log C_M = -3$

$$\log S = 11 - 2pH$$

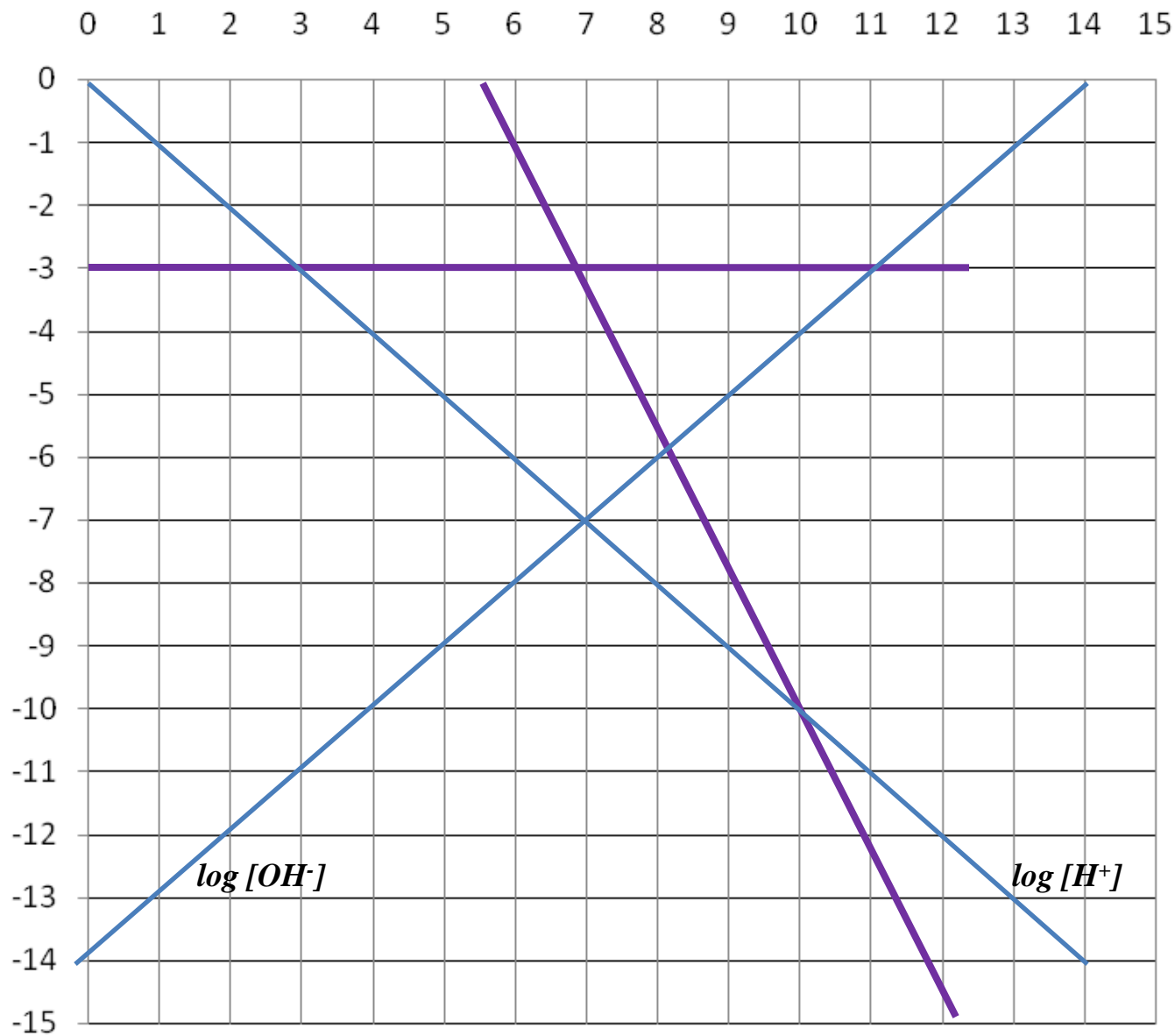


log S'

pH

Para el Níquel:
 $\log C_M = -3$

$\log S = 11 - 2pH$

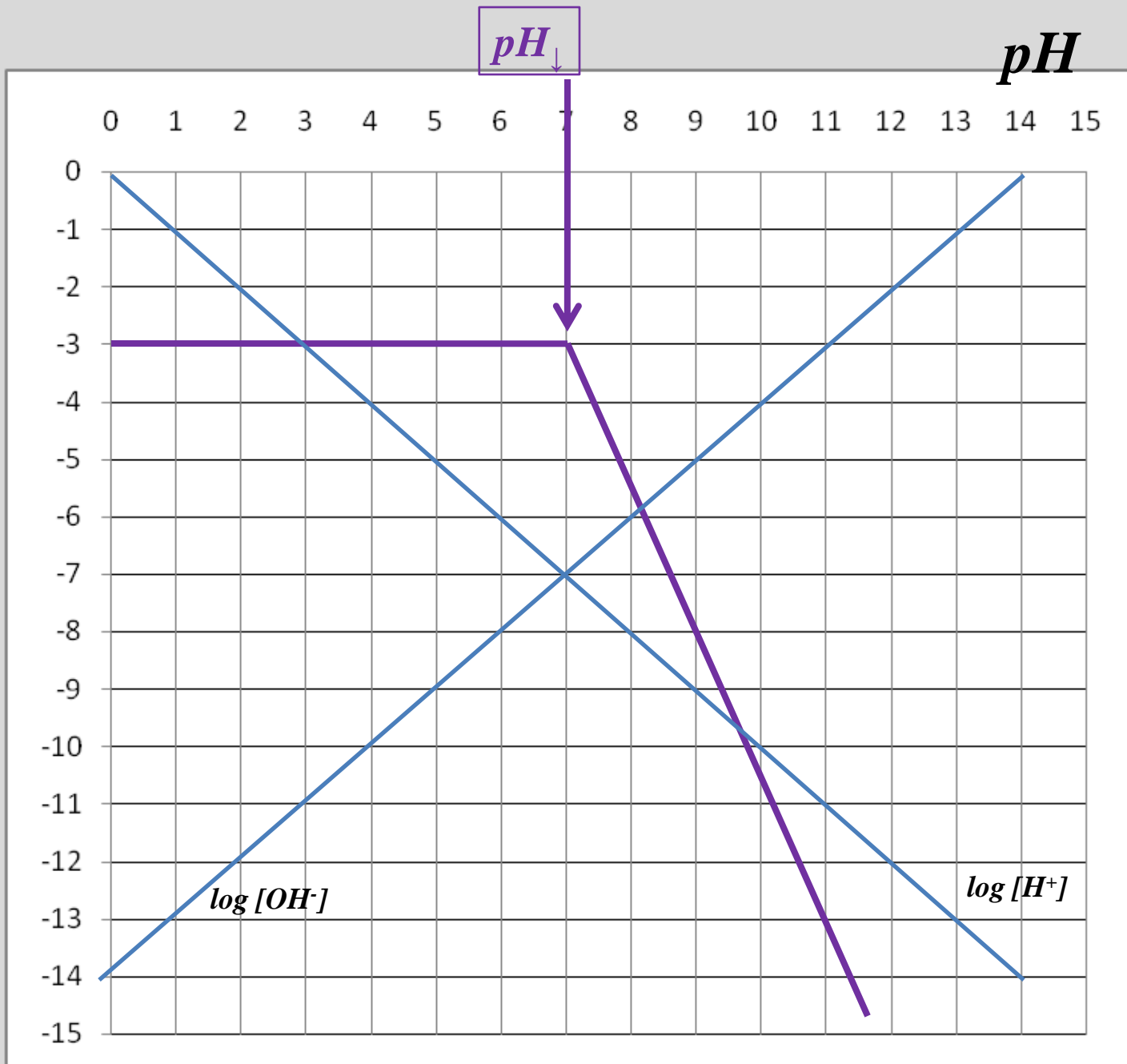


$\log S'$

Para el Níquel:
 $\log C_M = -3$

$$\log S = 11 - 2pH$$

$\log S'$



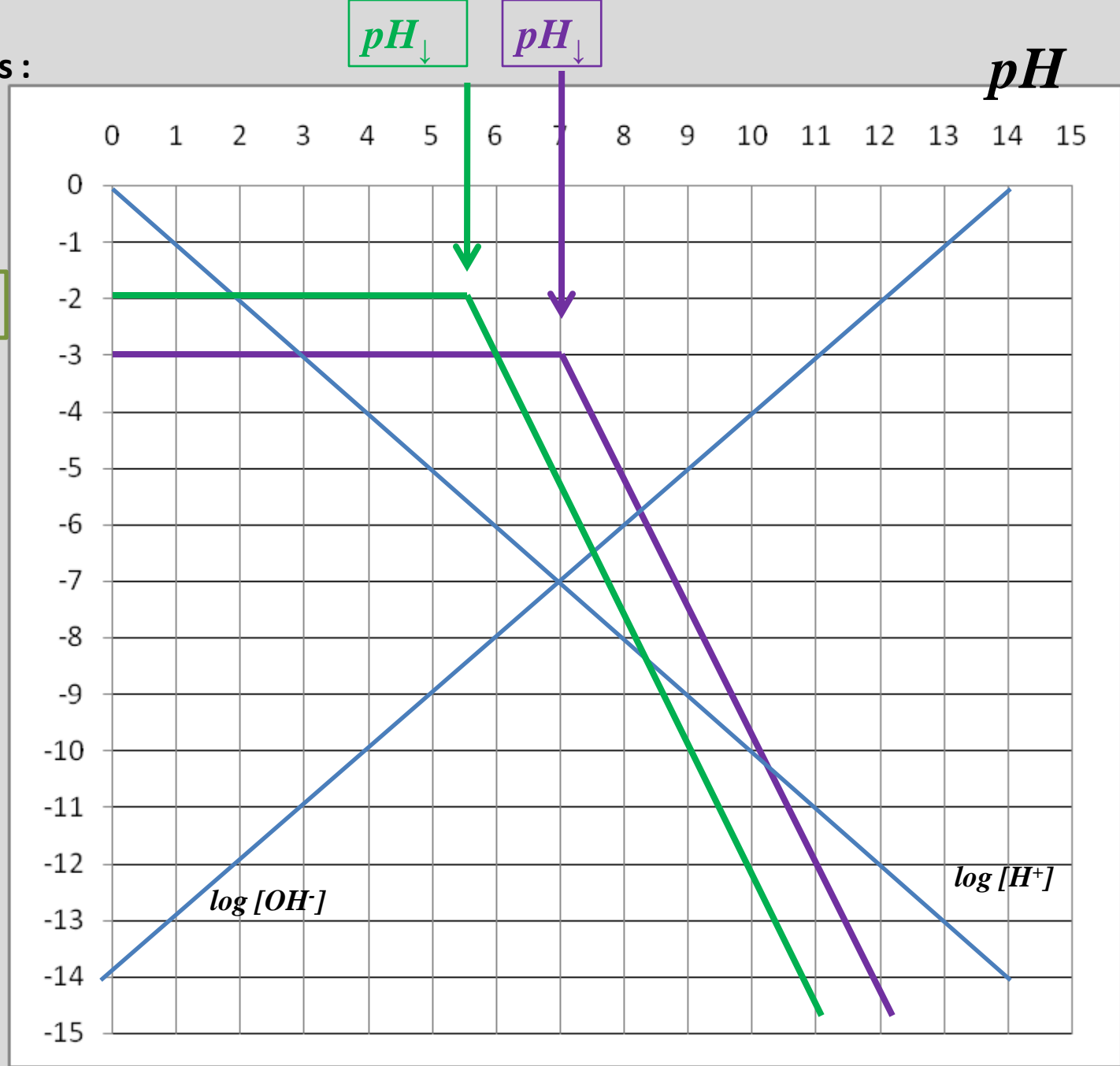
Para ambos cationes :

$\log C_{Cd} = -2$

$\log C_{Ni} = -3$

$\log S = 9 - 2pH$

$\log S = 11 - 2pH$

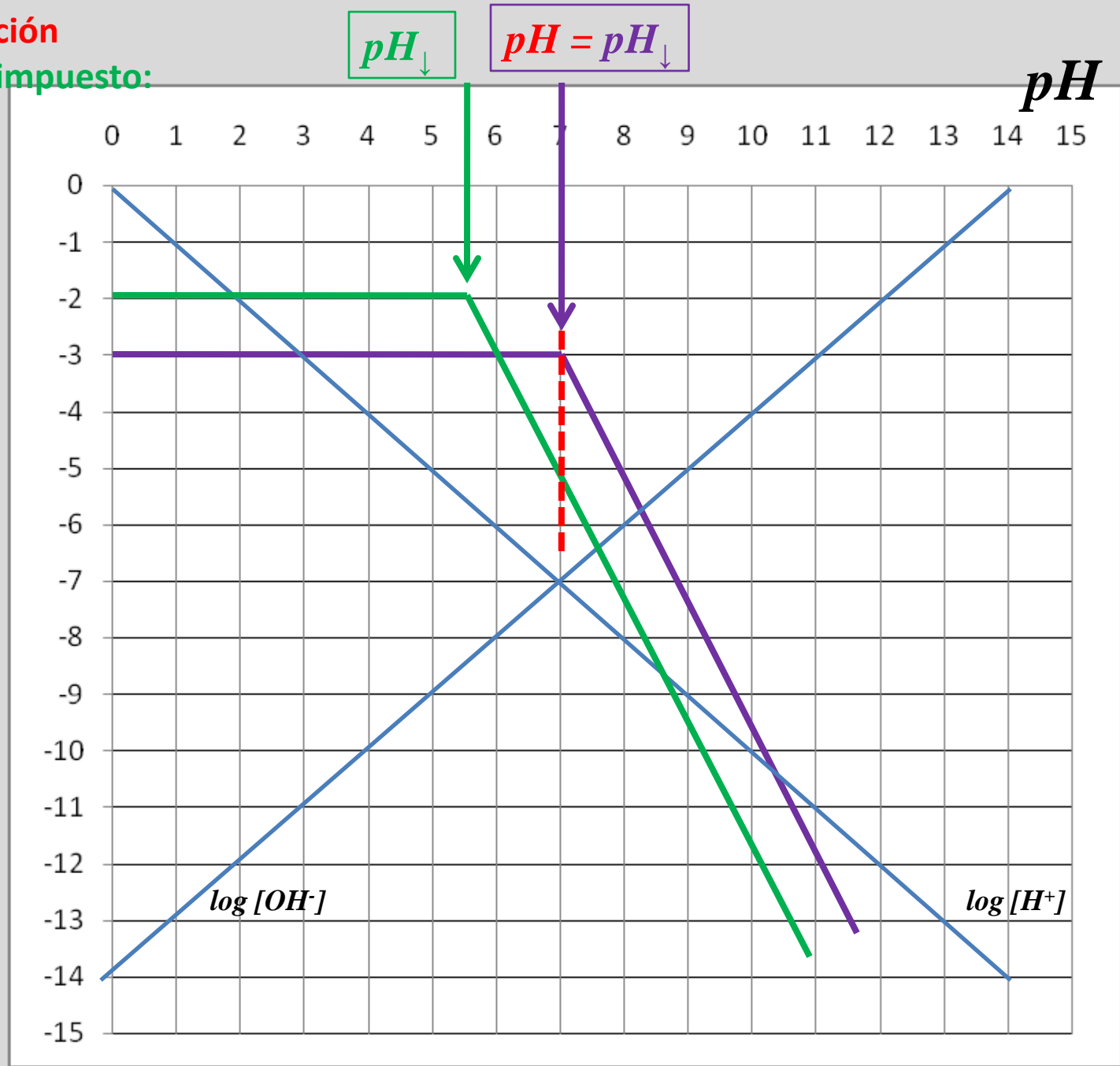


$\log S'$

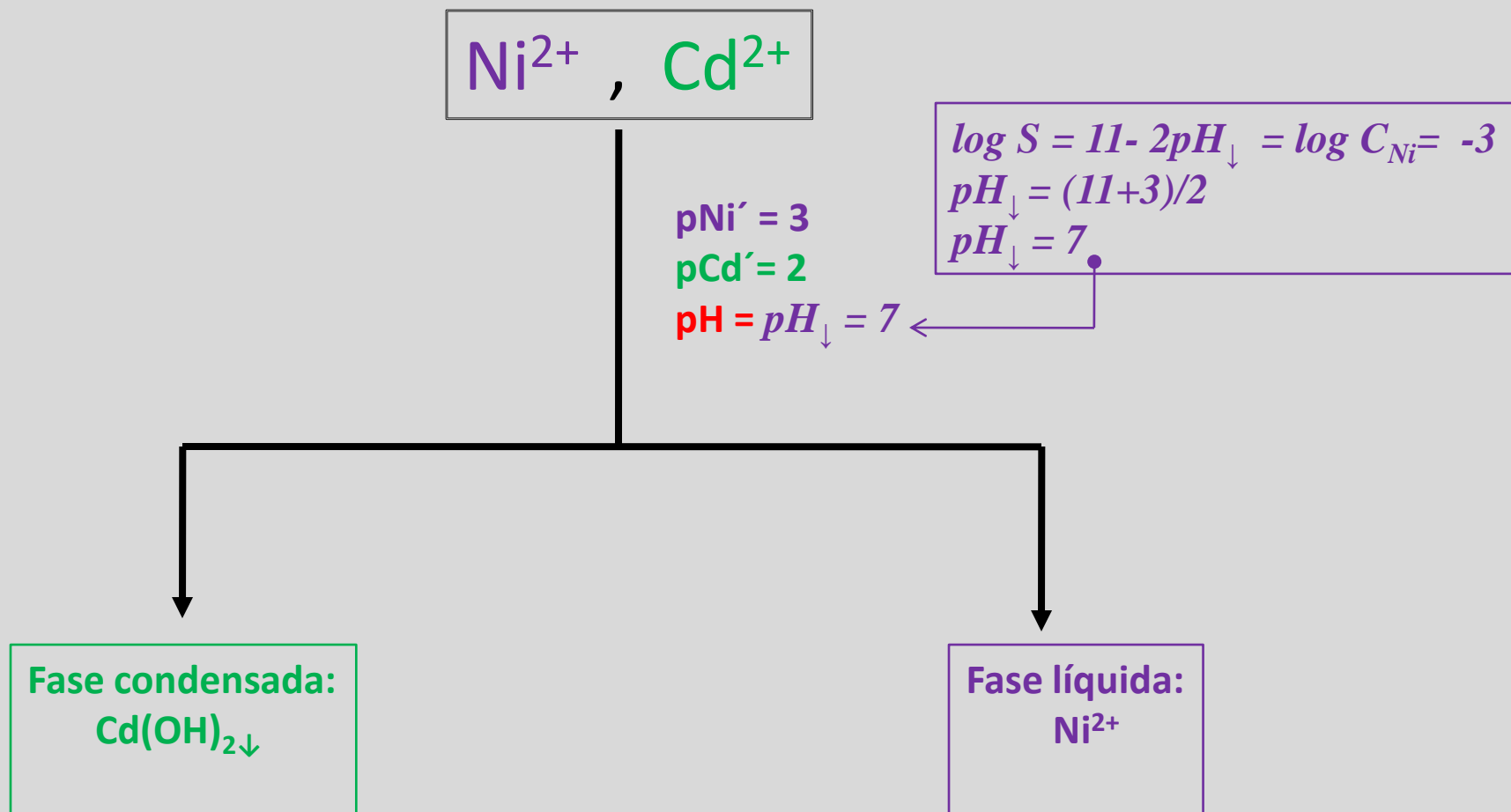
Esquema de separación
en una etapa a pH impuesto:

$\log C_{Cd} = -2$
 $\log C_{Ni} = -3$

$\log S'$



Esquema de separación en una etapa a pH impuesto:



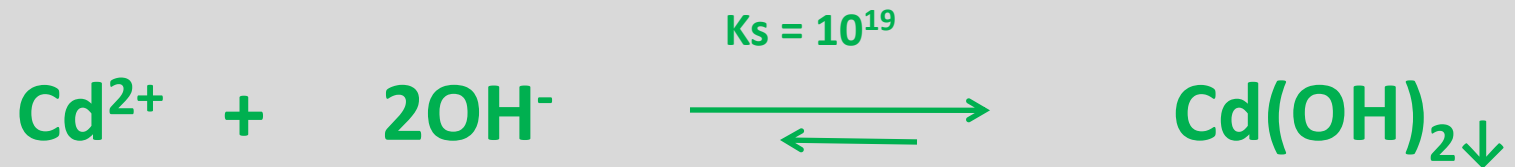
A partir de $pH = pH_{\downarrow}$:

Definición de parámetro adimensional de operación analítica, f :

$$f = \frac{n_{precipitada}}{n_0}$$

$$A \quad pH = pH_{\downarrow} :$$

Reacción *operativa* de precipitación:



Inic. C_M

$$f = \frac{n_{precipitada}}{n_0}$$

$$A \quad pH = pH_{\downarrow} :$$

Reacción *operativa* de precipitación,
Tabla de variación de especies:



Inic. C_{Cd}

Agreg. fC_0

Equil. $C_{Cd}(1-f)$ fn_0

$$[Cd^{2+}] = C_{Cd}(1-f):$$



$$A \quad pH = pH_{\downarrow} :$$

Reacción *operativa* de precipitación,
Tabla de variación de especies:



Inic. C_{Cd}

Agreg. fC_0

Equil. $C_{Cd}(1-f)$

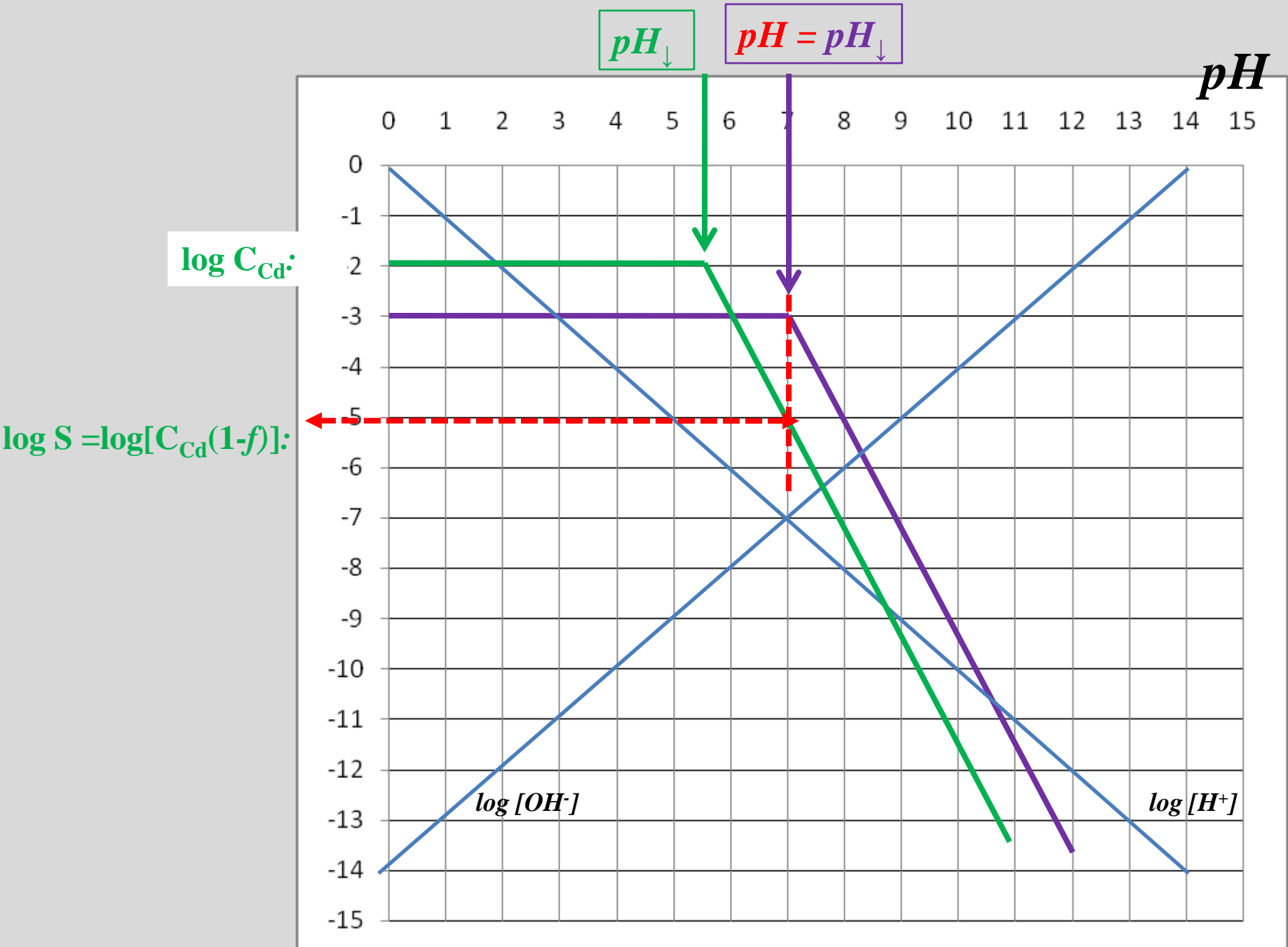
fn_0



$$S = [Cd^{2+}] = C_{Cd}(1-f):$$



“cuando empieza a precipitar el Ni, pH_{\downarrow} ,
queda en solución $S = [Cd^{2+}] = C_{Cd}(1-f)$ ”



De la tabla de variación de especies:

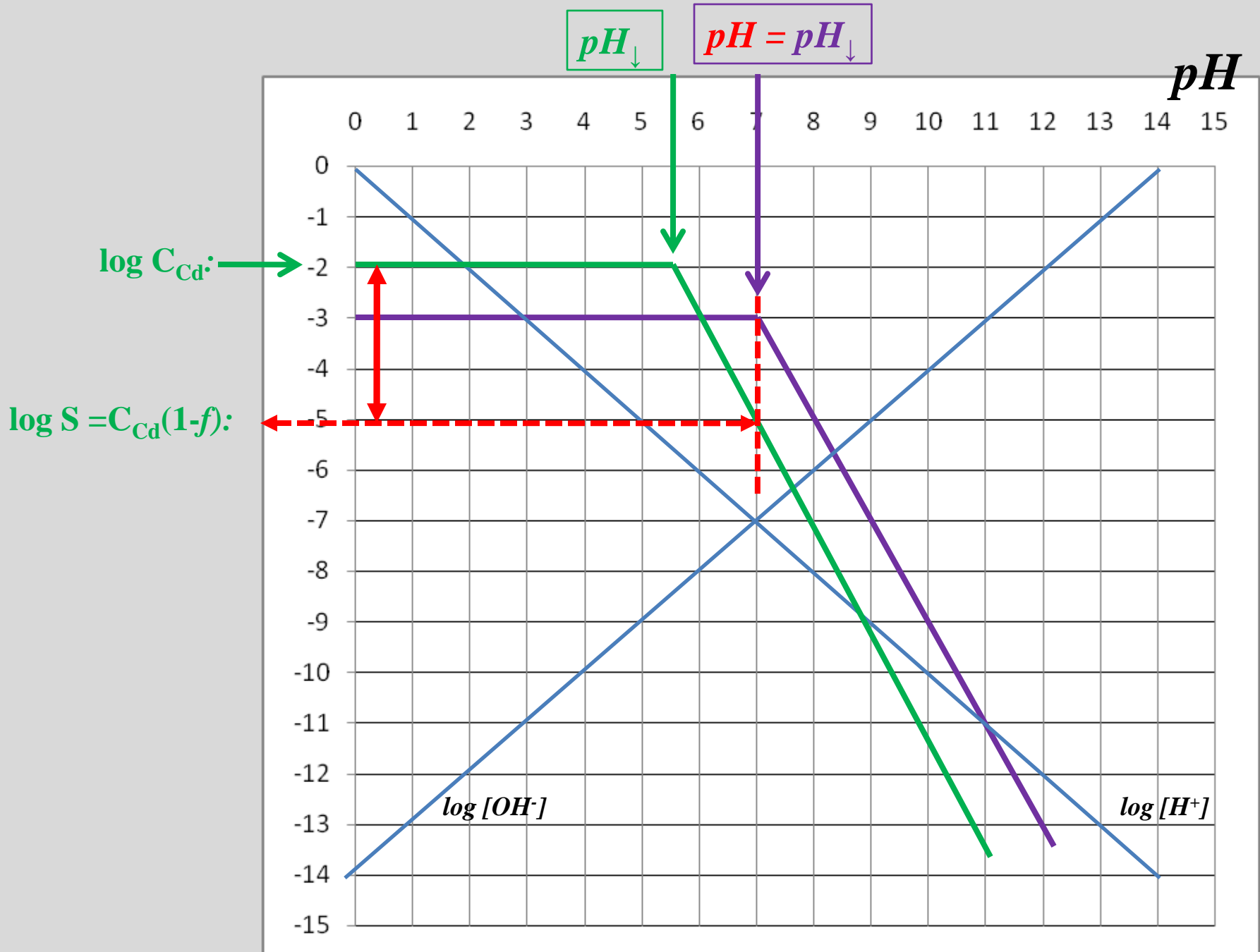
$$\log S = \log [C_{Cd}(1-f)]$$

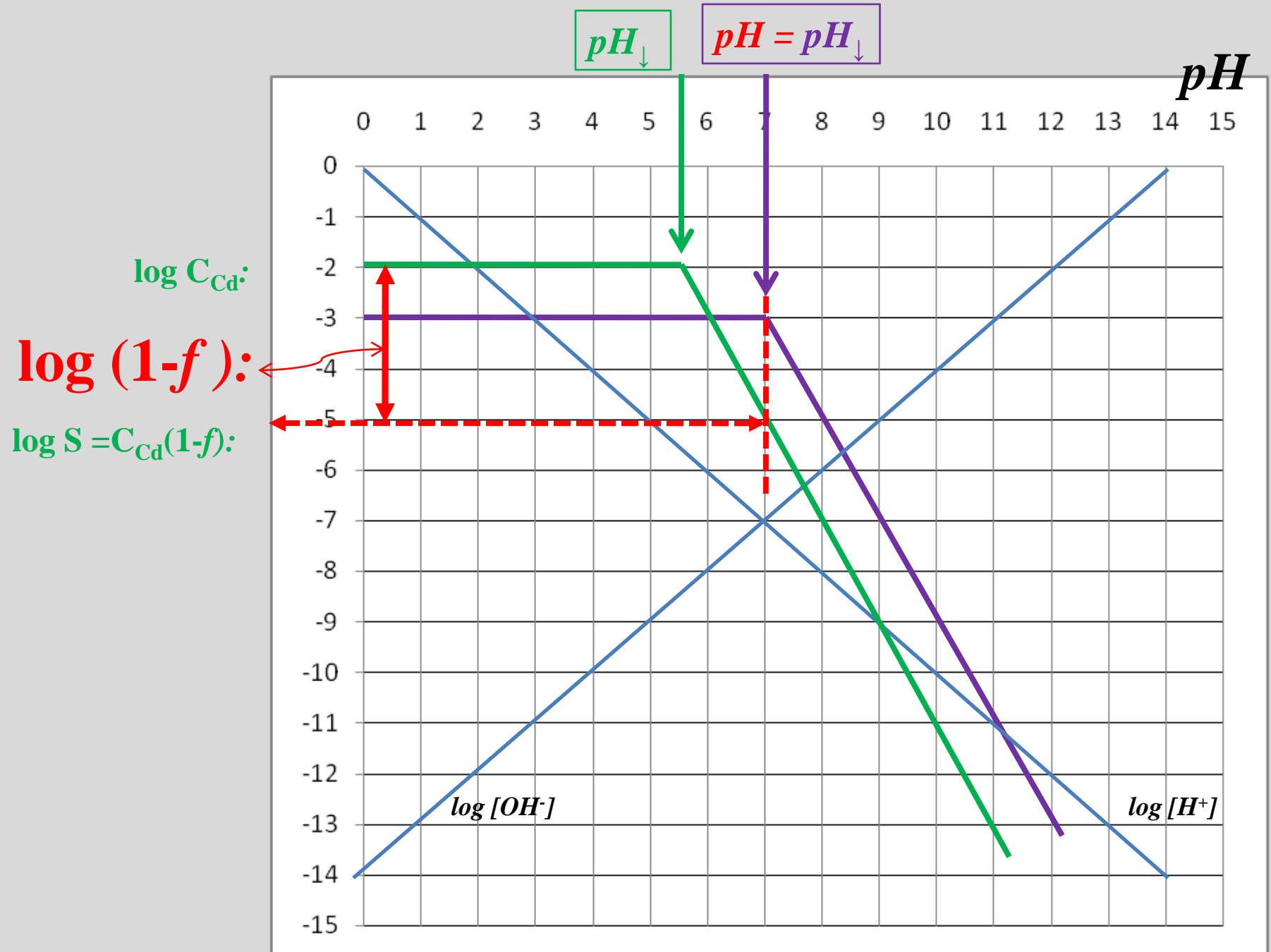
$$\log (1-f) = \log S - \log C_{Cd}$$

$$\log S = \log [C_{Cd}(1-f)]$$

$$\log (1-f) = \log S - \log C_{Cd}$$

Gráficamente:





Gráficamente:

$$\log (1-f) \approx -3$$

$$f = 1 - 10^{-3} = 1 - 0.001$$

$$f = 0.999; \quad f\% = 99.90\%$$

Algebraicamente:

Para el níquel:

$$K_s = [\text{Ni}^{2+}][\text{OH}^-]^2 = 10^{-17};$$

$$\text{A } \text{pH}_{\downarrow} = 7.0, \quad \text{pOH}_{\downarrow} = 7.0$$

$$C_{\text{Ni}} [\text{OH}^-]^2 = 10^{-17}$$

$$(10^{-3})(10^{-7})^2 = 10^{-17} = K_s.$$

Algebraicamente:

Para el cadmio:

$$K_s = [\text{Cd}^{2+}][\text{OH}^-]^2 = 10^{-19};$$

$$\text{A } \text{pH}_{\downarrow} = 7.0, \quad \text{pOH}_{\downarrow} = 7.0$$

$$S[\text{OH}^-]^2 = 10^{-19}$$

$$(S)(10^{-7})^2 = 10^{-19}$$

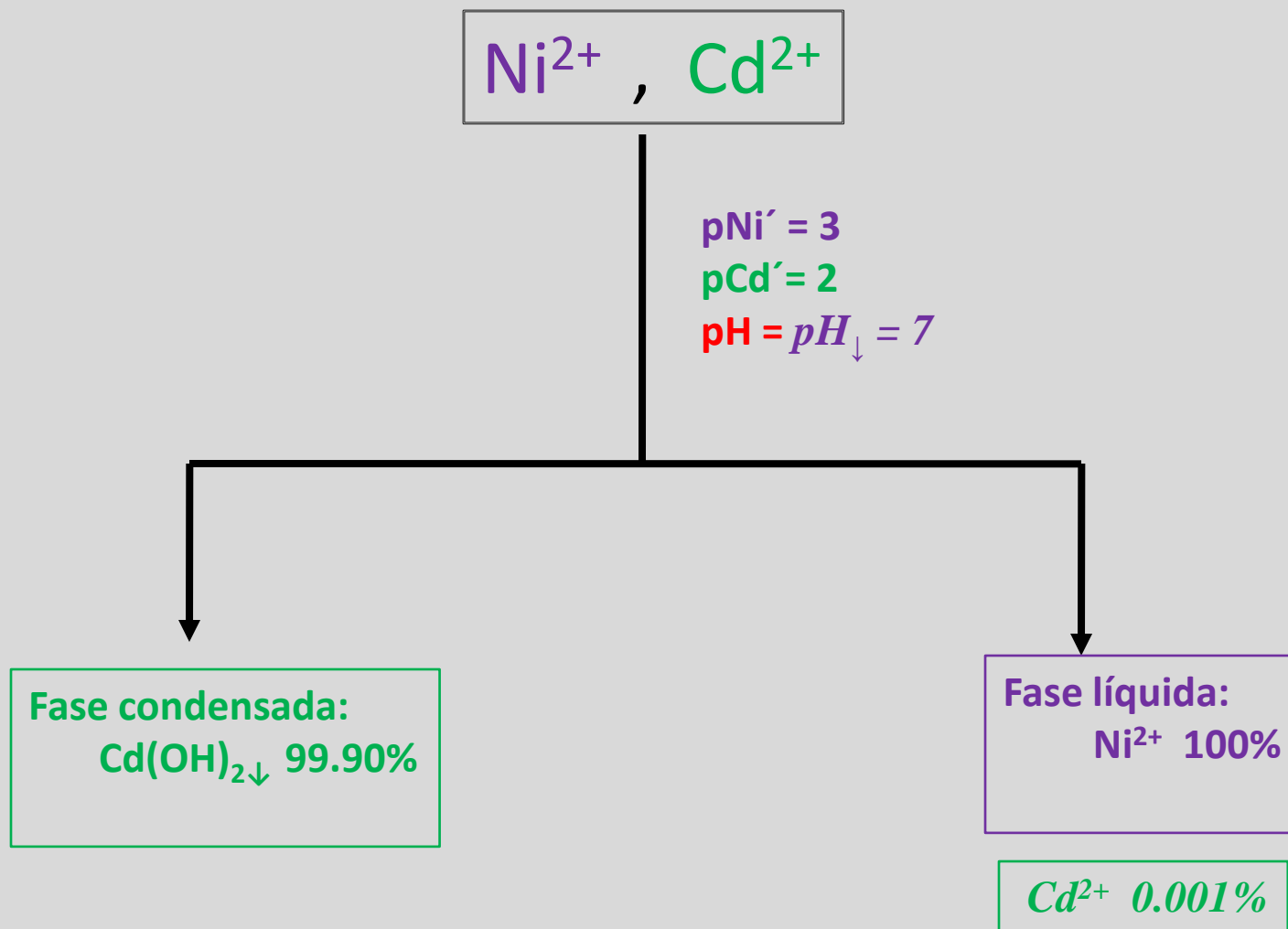
$$S = 10^{-5} \text{ mol/L}$$

$$1-f = (S/C_{\text{Cd}}) = (10^{-5}/10^{-2}) = 10^{-3}$$

$$f = 1 - 0.001 = 0.999$$

$$f \% = 99.90\%$$

Esquema de separación en una etapa a pH impuesto:



Bibliografía de apoyo:

James Newton Butler
“Solubility and pH Calculations”
Addison-Wesley Publishing Company, Inc.
1964

Yu. S. Lyalikov, Yu. A. Klyachko
“Theoretical Foundations of Modern Chemical Analysis”
Mir Publishers , Moscow .
1980.

Santiago Vicente Pérez
“Química de las Disoluciones. Diagramas y Cálculos Gráficos”
Alhambra.
1985.

A. Baeza
“Química Analítica. Expresión Gráfica de las Reacciones Químicas”
S. Y G. Editores.
2006.