Universidad Nacional Autónoma de México

Facultad de Química

Química Inorgánica I

6. Óxido-reducción

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Víctor Fabián Ruiz Ruiz.

Reacción de oxidación y reducción:

$$Zn + 2HCl \rightarrow ZnCl_2 + H_2$$

$$Zn + 2H^+ \rightarrow Zn^{2+} + H_2$$

$$2H^+ + 2e \rightarrow H_2 \qquad \text{Reducción}$$

$$Zn^{2+} + 2e \rightarrow Zn \qquad \text{Oxidación x “-1”}$$

$2H^+ + 2e \rightarrow H_2$ $\quad \Delta G^\circ_{Re}$ $\quad \Delta G^\circ_{Re} = -n_{eRe}FE^\circ_{Re}$

$Zn^{2+} + 2e \rightarrow Zn^{2+} + 2e$ $\quad -\Delta G^\circ_{Ox}$ $\quad \Delta G^\circ_{Ox} = -n_{eOx}FE^\circ_{Ox}$

$\Delta G^\circ r = \Delta G^\circ_{Re} - \Delta G^\circ_{Ox}$ $\quad \Delta G = -n_e F E N_A E$

$\Delta G^\circ r = -n_e F E^\circ_{cel} = -n_{eRe}FE^\circ_{Re} - (-n_{eOx}FE^\circ_{Ox})$

$E^\circ_{cel} = E^\circ_{Re} - (E^\circ_{Ox})$

$E^\circ_{cel} = E^\circ_{H+/H2} - (E^\circ_{Zn2+/Zn}) = 0.76\ V$

$\Delta G^\circ r < 0;\ E^\circ_{cel} > 0;\ E^\circ_{H+/H2} > E^\circ_{Zn2+/Zn}$

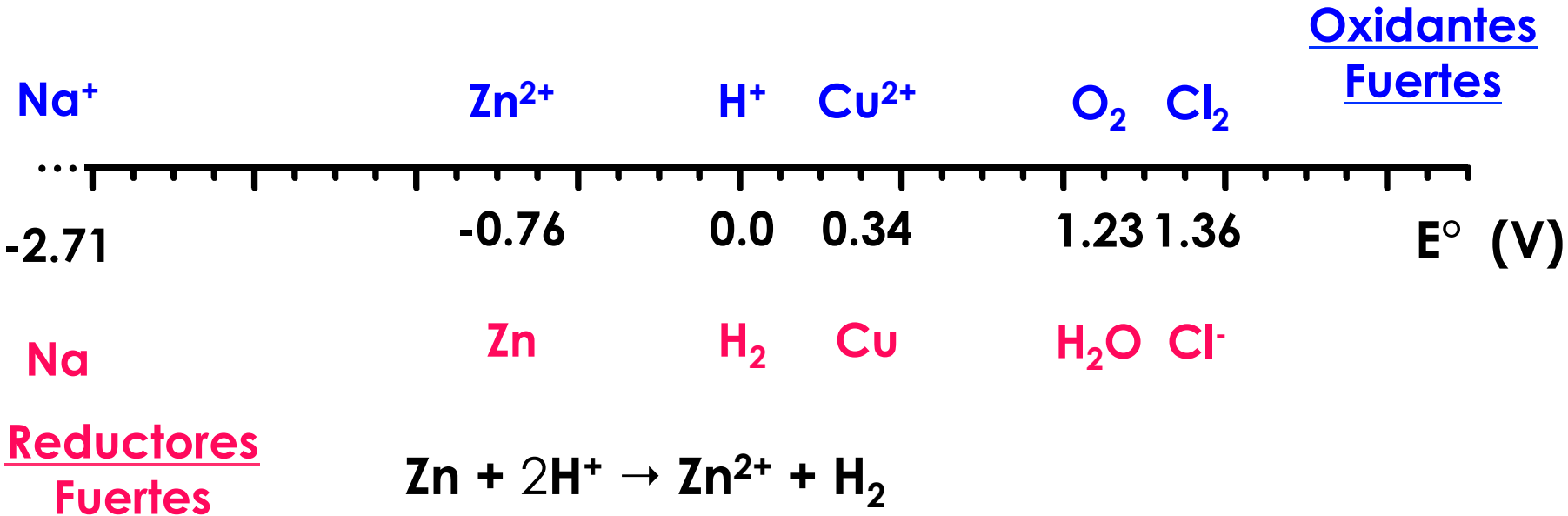
Si

$E^\circ_{H+/H2} = 0\ V$

$E^\circ_{cel} = -(E^\circ_{Zn2+/Zn})$

Especie o "versión" **oxidada**, **oxidante**

Especie o "versión" **reducida**, **reductor**



$Zn + 2H^+ \rightarrow Zn^{2+} + H_2$

$ClO_4^- + 2\,H^+ + 2\,e \rightleftharpoons ClO_3^-\,H_2O$ 1.189

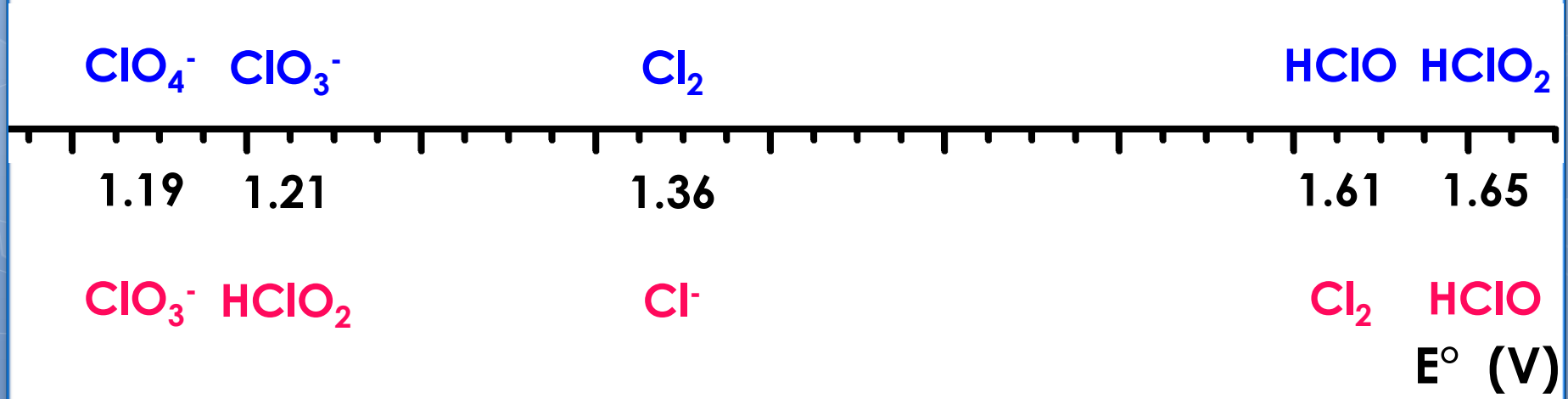
$ClO_3^- + 3\,H^+ + 2\,e \rightleftharpoons HClO_2 + H_2O$ 1.214

$Cl_2(g) + 2\,e \rightleftharpoons 2\,Cl^-$ 1.35827

$HClO + H^+ + e \rightleftharpoons 1/2\,Cl_2 + H_2O$ 1.611

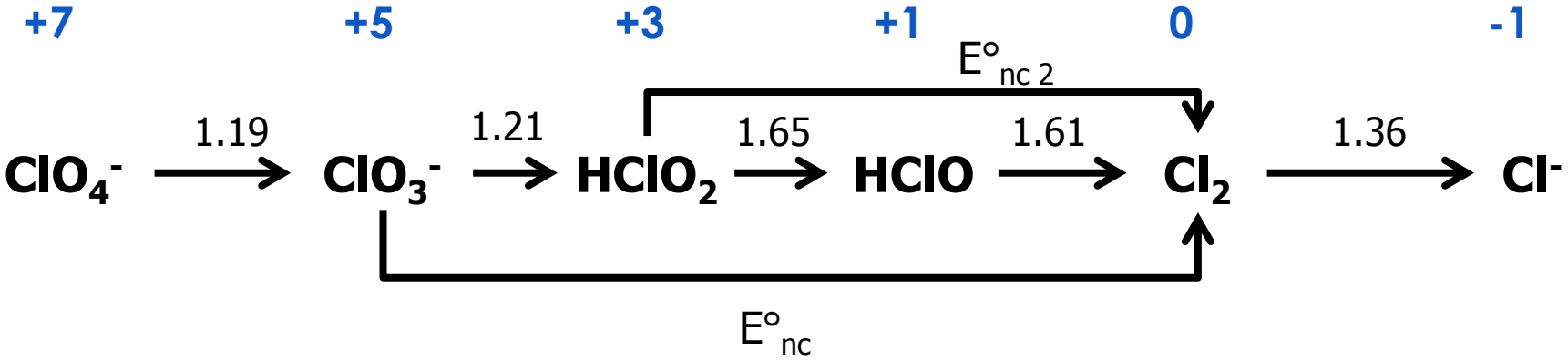
$HClO_2 + 2\,H^+ + 2\,e \rightleftharpoons HClO + H_2O$ 1.645

$H^+ + \mathbf{HClO} + \mathbf{Cl^-} \rightarrow H_2O + \mathbf{Cl_2} + \mathbf{Cl_2}$



Diagramas de Latimer:

$ClO_4^- + 2\,H^+ + 2\,e \rightleftharpoons ClO_3^-\,H_2O$	1.189
$ClO_3^- + 3\,H^+ + 2\,e \rightleftharpoons HClO_2 + H_2O$	1.214
$HClO_2 + 2\,H^+ + 2\,e \rightleftharpoons HClO + H_2O$	1.645
$HClO + H^+ + e \rightleftharpoons 1/2\,Cl_2 + H_2O$	1.611
$Cl_2(g) + 2\,e \rightleftharpoons 2\,Cl^-$	1.35827



Diagramas de Latimer:

$3H^+ + ClO_3^- + 2e \rightarrow HClO_2 + H_2O$ $\quad \Delta G°_1 = (2e)F\ E°_1$

$2H^+ + HClO_2 + 2e \rightarrow HClO + H_2O$ $\quad \Delta G°_2 = (2e)F\ E°_2$

$H^+ + HClO + 1e \rightarrow \frac{1}{2}\ Cl_2 + H_2O$ $\quad \Delta G°_3 = (1e)F\ E°_3$

$6H^+ + ClO_3^- + 5e \rightarrow \frac{1}{2}\ Cl_2 + 3H_2O$ $\quad \Delta G°_{nc} = (5e)F\ E°_{nc}$

$$\Delta G°_{nc} = \Delta G°_1 + \Delta G°_2 + \Delta G°_3$$

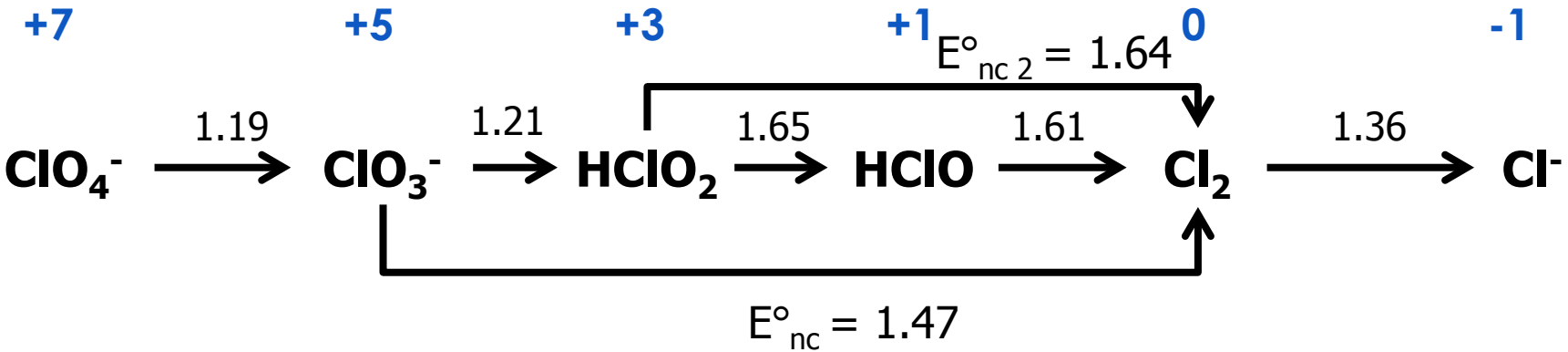
$$(5e)FE°_{nc} = (2e)F\ E°_1 + (2e)F\ E°_2 + (1e)F\ E°_3$$

$$E°_{nc} = (\ (2e)\ E°_1 + (2e)\ E°_2 + (1e)\ E°_3\ ) / (5e)$$

$$E°_{nc} = 1.47\ V$$

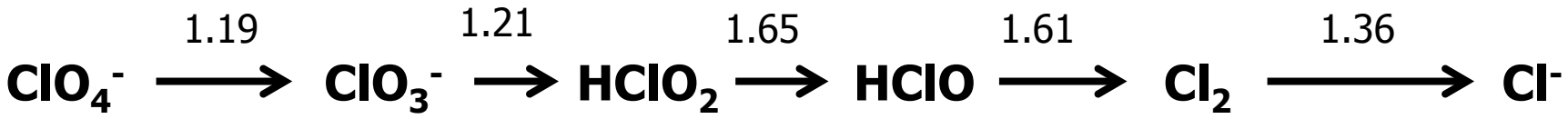
Diagramas de Latimer:

$ClO_4^- + 2\,H^+ + 2\,e \rightleftharpoons ClO_3^-\,H_2O$	1.189
$ClO_3^- + 3\,H^+ + 2\,e \rightleftharpoons HClO_2 + H_2O$	1.214
$HClO_2 + 2\,H^+ + 2\,e \rightleftharpoons HClO + H_2O$	1.645
$HClO + H^+ + e \rightleftharpoons 1/2\,Cl_2 + H_2O$	1.611
$Cl_2(g) + 2\,e \rightleftharpoons 2\,Cl^-$	1.35827



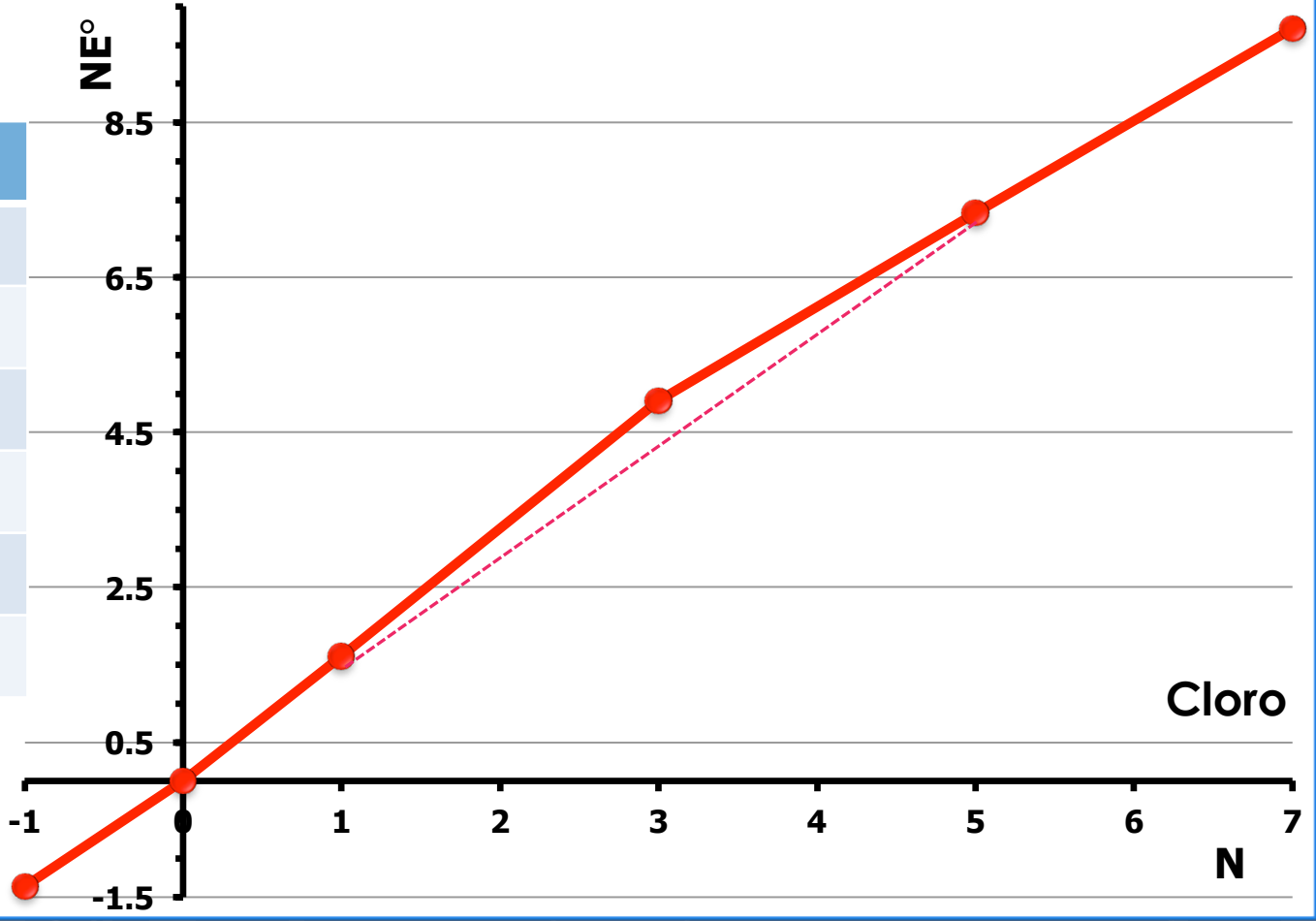
Diagramas de Frost:

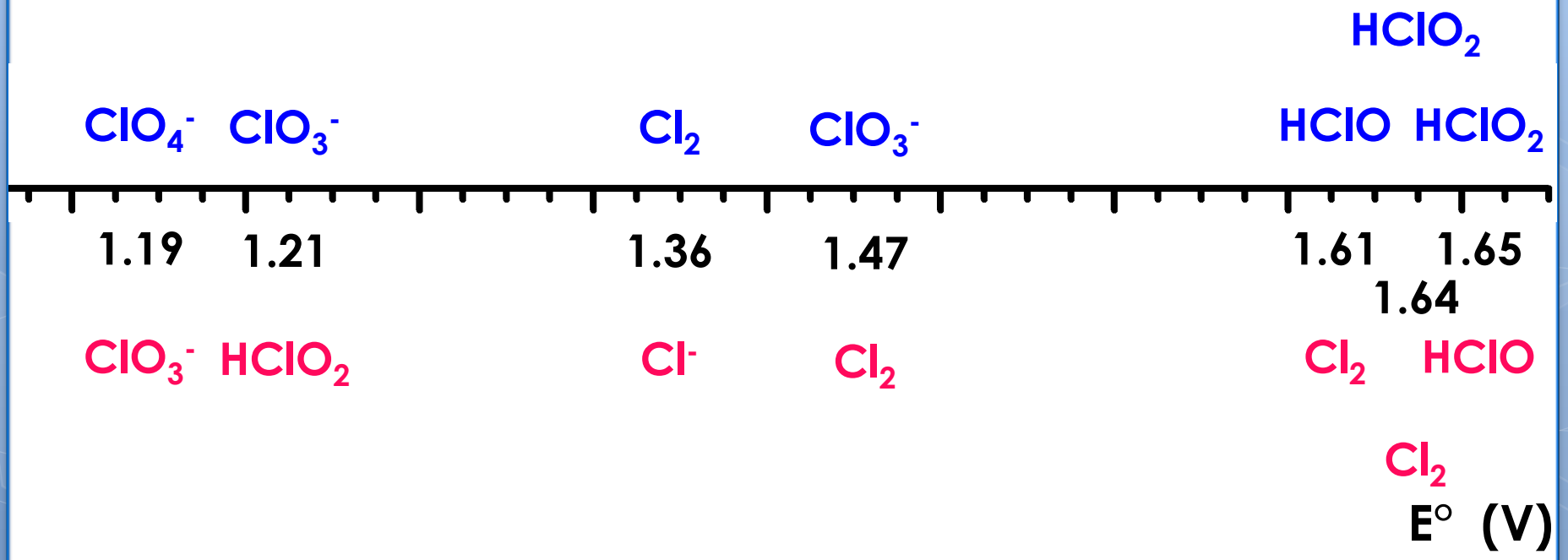
N	NE°
-1	
0	0
1	
3	
5	
7	



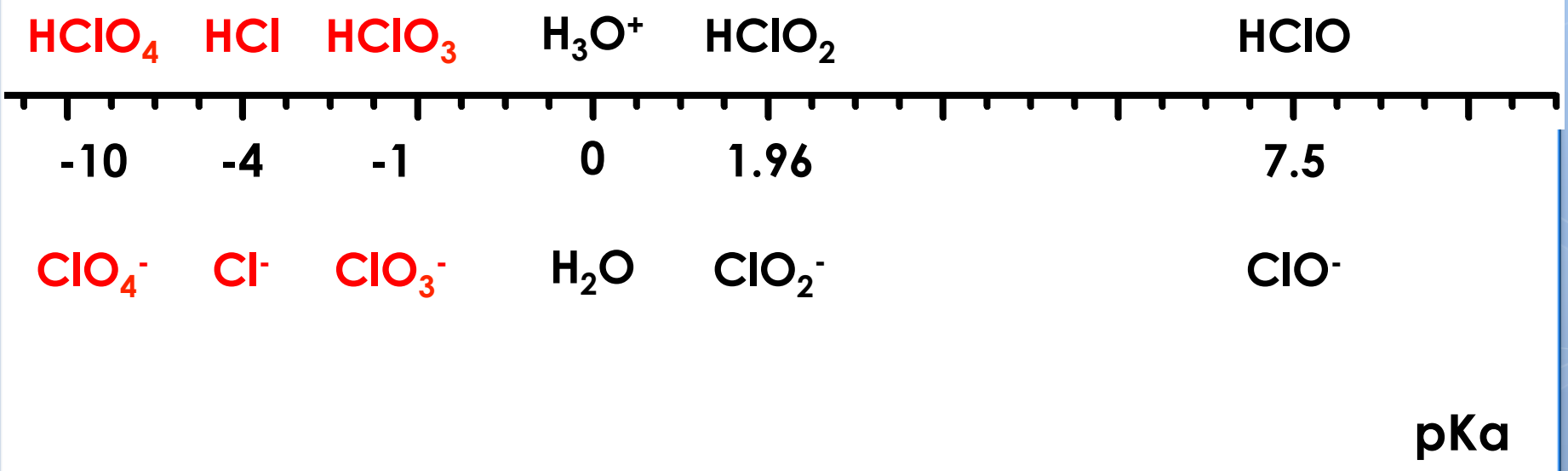
Diagramas de Frost:

N	NE°
-1	
0	0
1	
3	
5	
7	

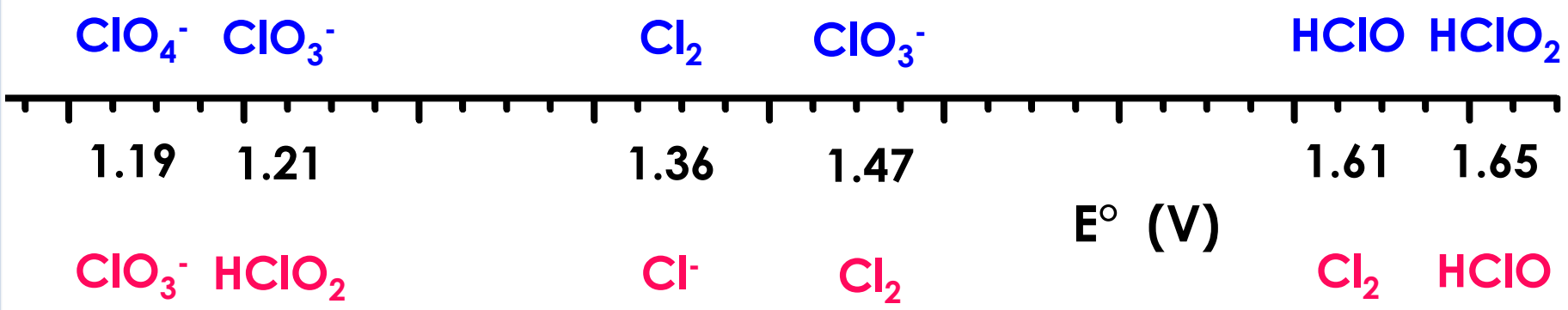



$HClO_2$
ClO_4^- ClO_3^- Cl_2 ClO_3^- HClO $HClO_2$
1.19 1.21 1.36 1.47 1.61 1.65
1.64
ClO_3^- $HClO_2$ Cl^- Cl_2 Cl_2 HClO
Cl_2
E° (V)

Influencia del pH:



Influencia del pH:



$$2H^+ + 2HClO + 2e \leftrightarrows Cl_2 + 2H_2O$$

$$Q = [Cl_2][H_2O]^2 / [HClO]^2[H^+]^2 \qquad \Delta G = -RT \ln Q$$

$$\Delta G = -RT \ln K - (- RT \ln Q) \qquad \Delta G° = -RT \ln K = -nFE°$$

$$-nFE = -nFE° + (RT) \ln Q \qquad E = E° - (RT/nF) \ln 10 \log Q$$

Influencia del pH:

$$2H^+ + 2HClO + 2e \leftrightarrows Cl_2 + 2H_2O$$

$$E = E^\circ - (RT/nF)\ \ln 10 \log Q$$

$$E = E^\circ - (RT/2F)\ \ln 10 \log ([Cl_2][H_2O]^2 / [HClO]^2[H^+]^2)$$

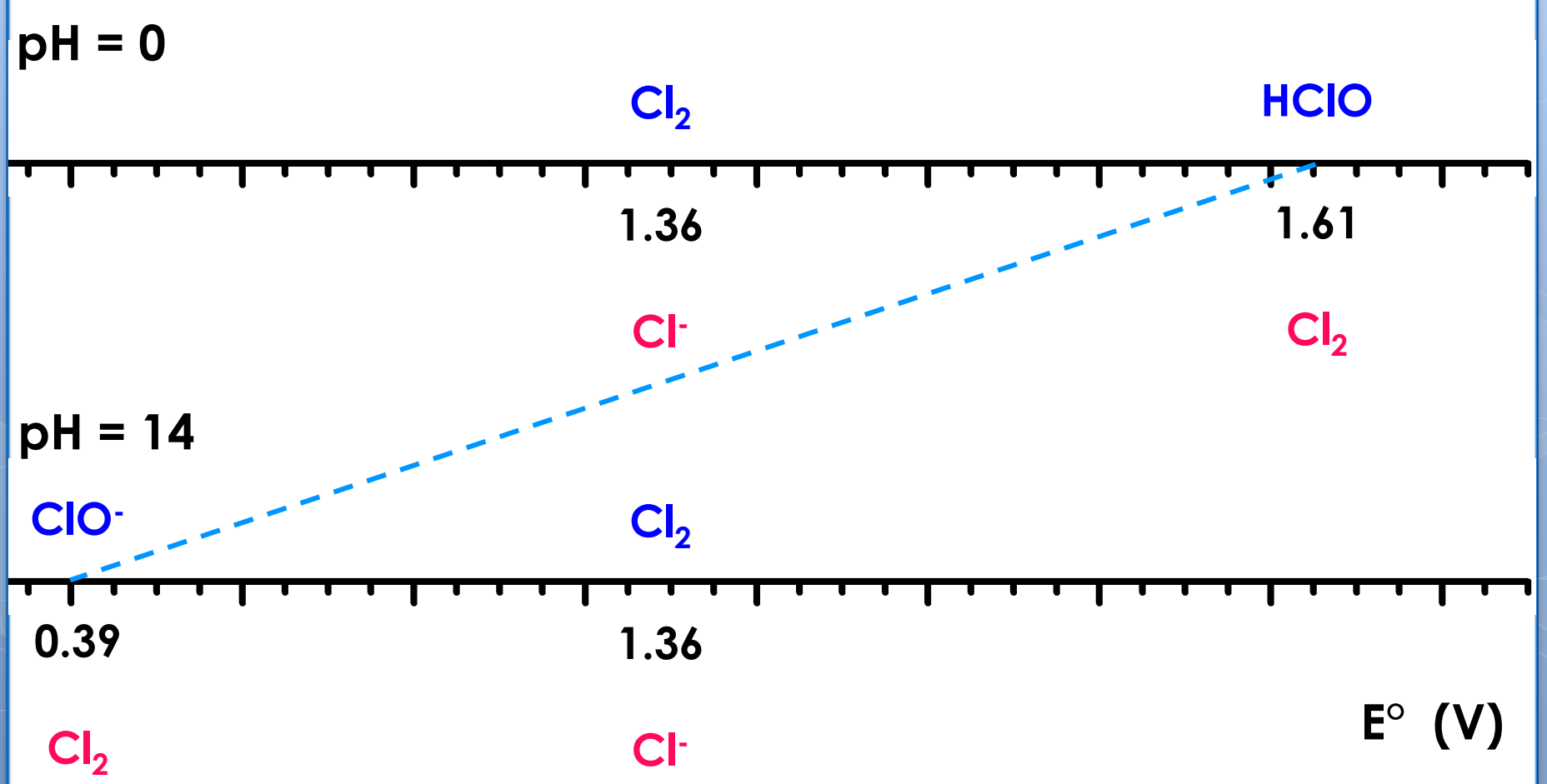
$$E = E^\circ - (0.059/2)(\log ([Cl_2][H_2O]^2 / [HClO]^2) - 2 \log[H^+])$$

$$E = E^\circ - (0.059/2)(\log ([Cl_2][H_2O]^2 / [HClO]^2) - 2(0.059/2)pH$$

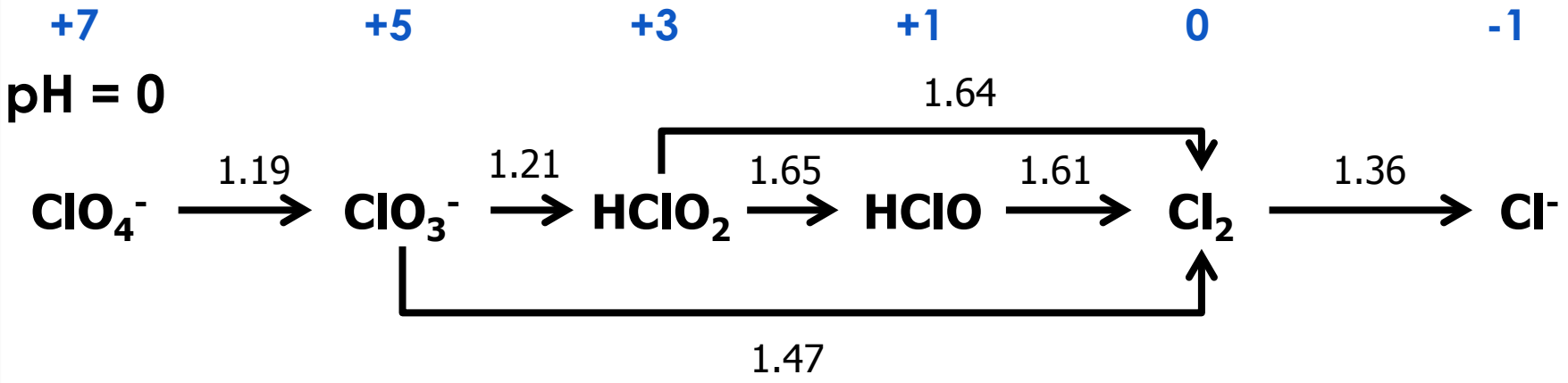
$$E\ (pH) = E^{\circ\prime} - 2(0.059/2)(pH)$$

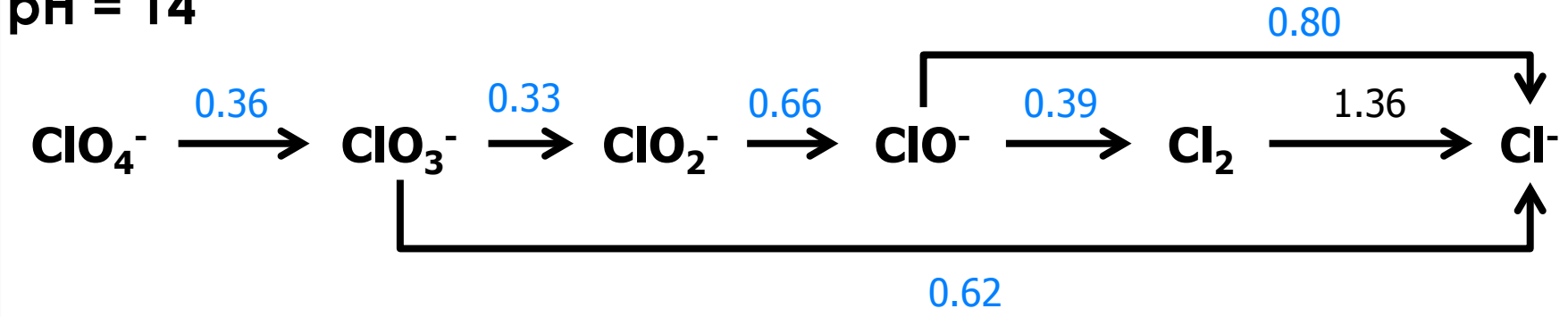
$$E\ (14) = 1.61 - 0.826 = 0.784\ V$$

Influencia del pH:



Diagramas de Latimer





Diagramas de Frost:

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-1	
0	0
1	
3	
5	
7