CAPACIDAD AMORTIGUADORA

DONALD D. VAN SLYKE

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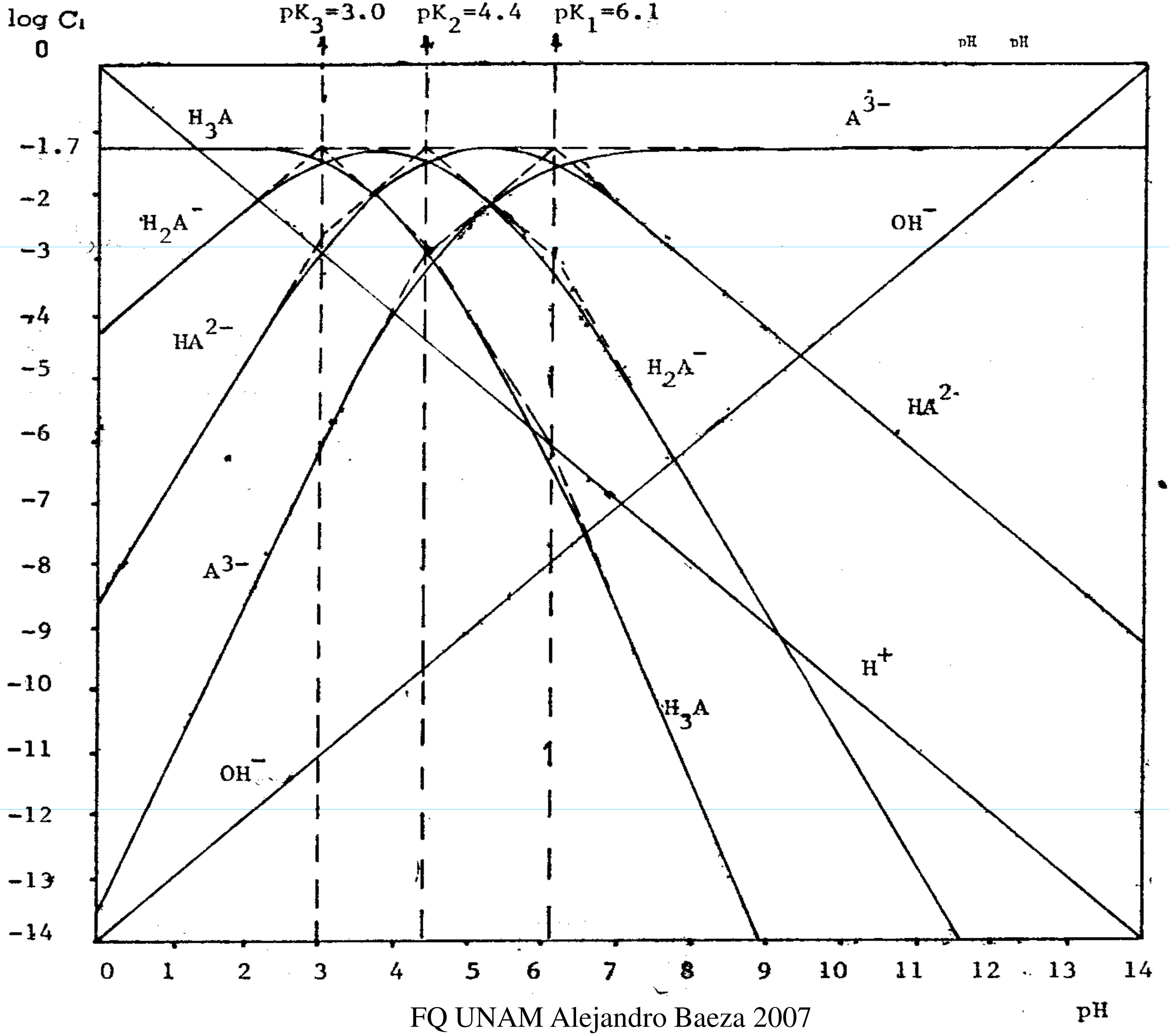
Química Analítica II

REBECA MARIANA SANDOVAL MÁRQUEZ



iagrama logarítmico de predominio de las especies del ácido cítrico en concent

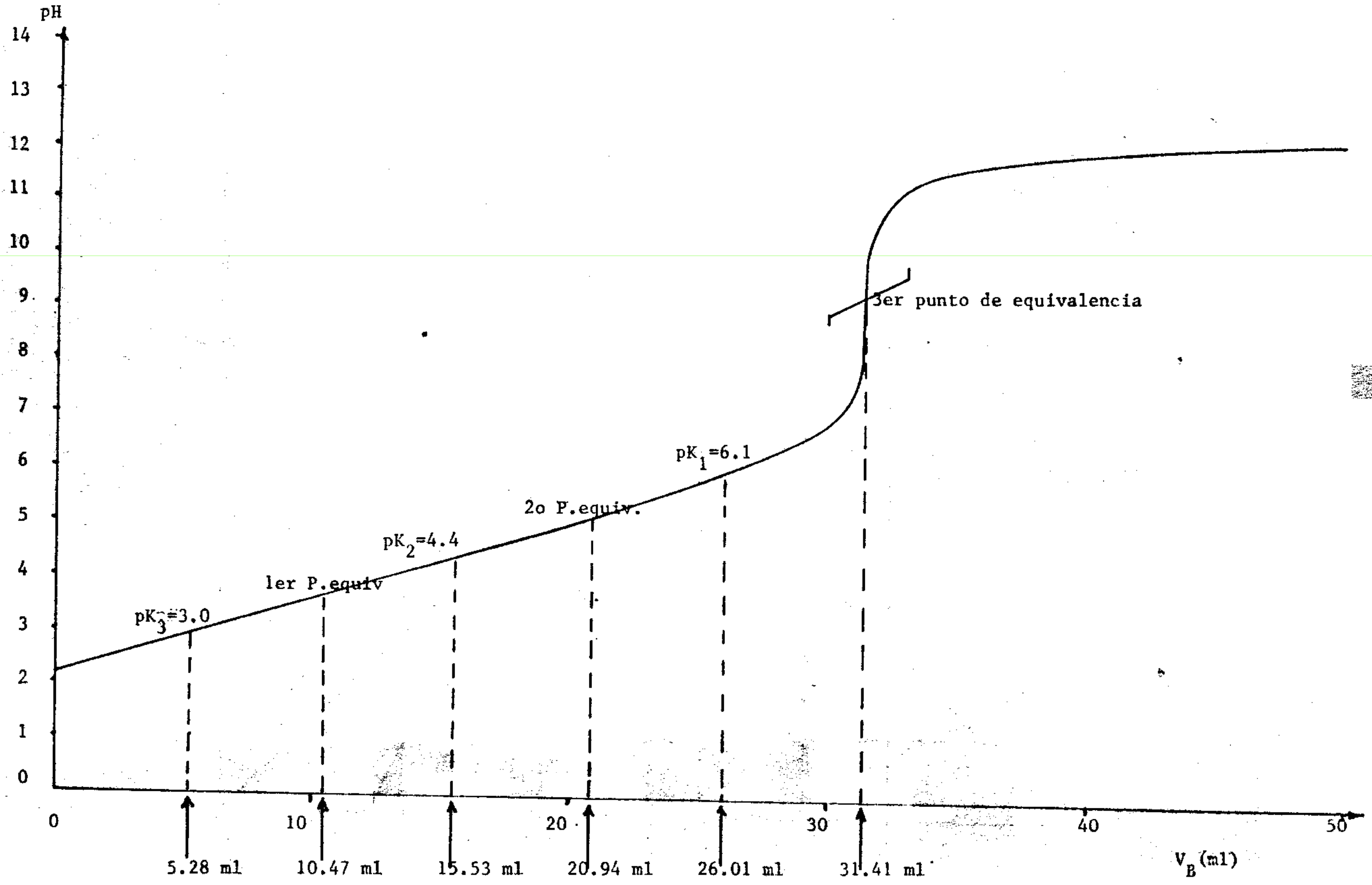
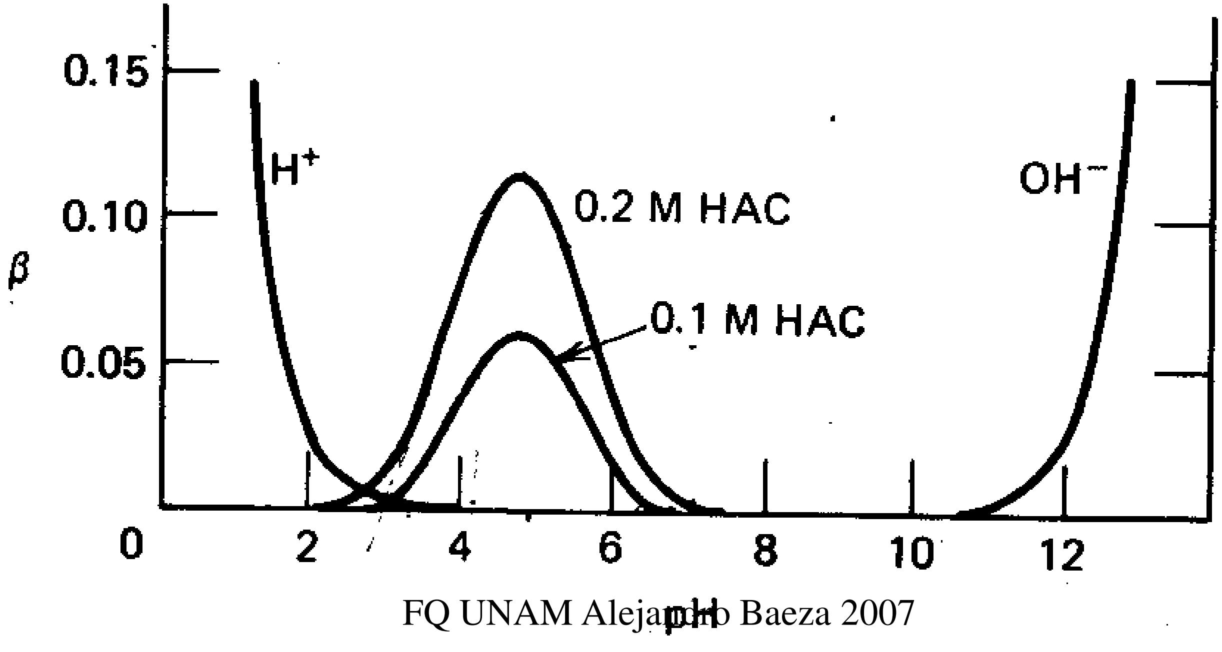


DIAGRAMA I.9. Curva de titulación potenciométrica, de 20 ml. de ácido cítrico 0.0504 M, con hidróxido de sodio 0.0963 M. Se tomó en cuenta la dilución y la curva es $pH = f(V_B)$.

$$\boxed{dB/d(\mathrm{pH}) = \beta = 2.303([\mathrm{H}^+] + [\mathrm{OH}^-]) \quad \text{for water}}$$

$$\frac{dB}{d(\mathrm{pH})} = \boxed{\beta = \frac{2.303\,K_a\,[\mathrm{H}^+][\mathrm{HA}]_0}{([\mathrm{H}^+] + K_a)^2}}$$



which agrees with the answer to Example 10 within the rounding-off error.

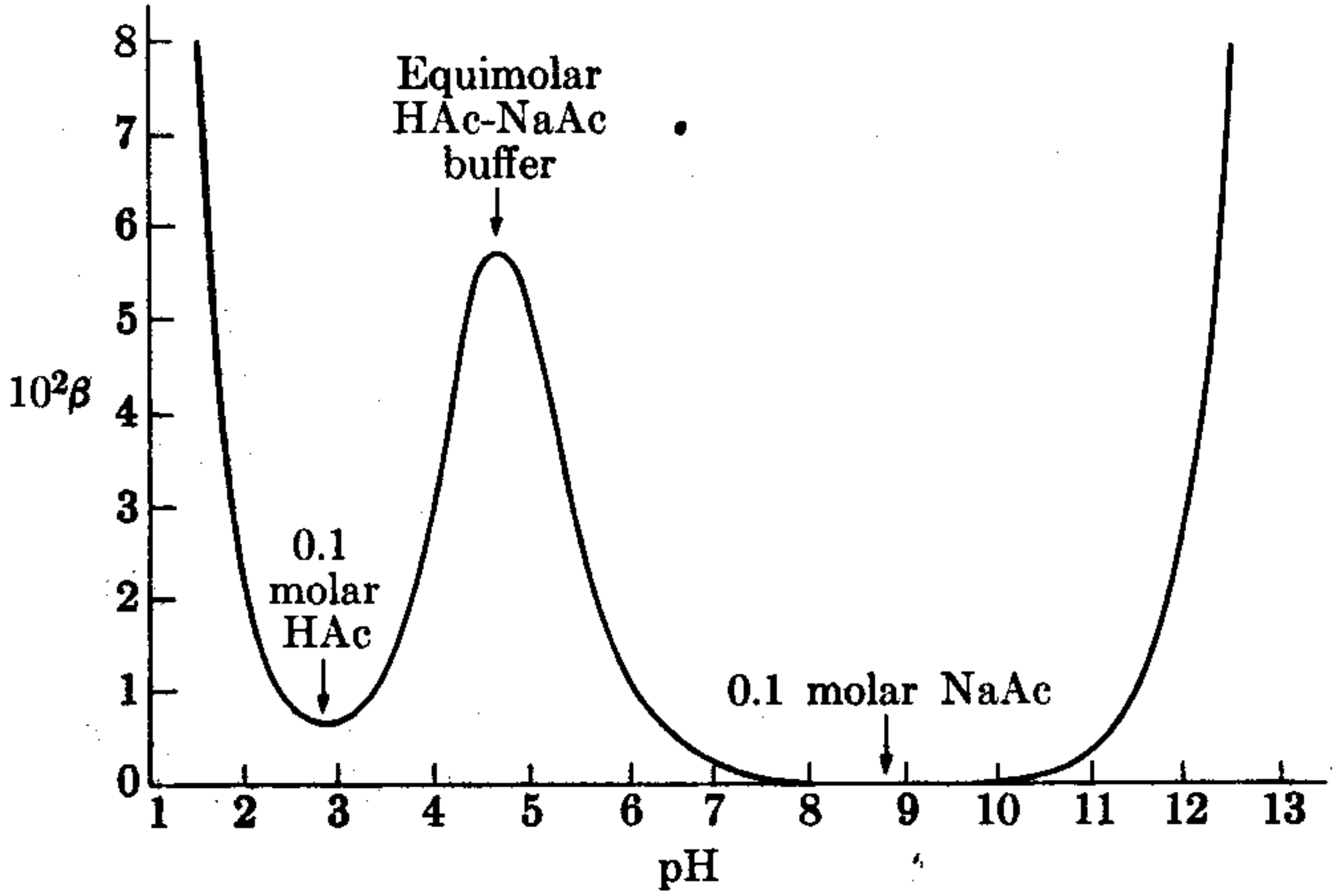
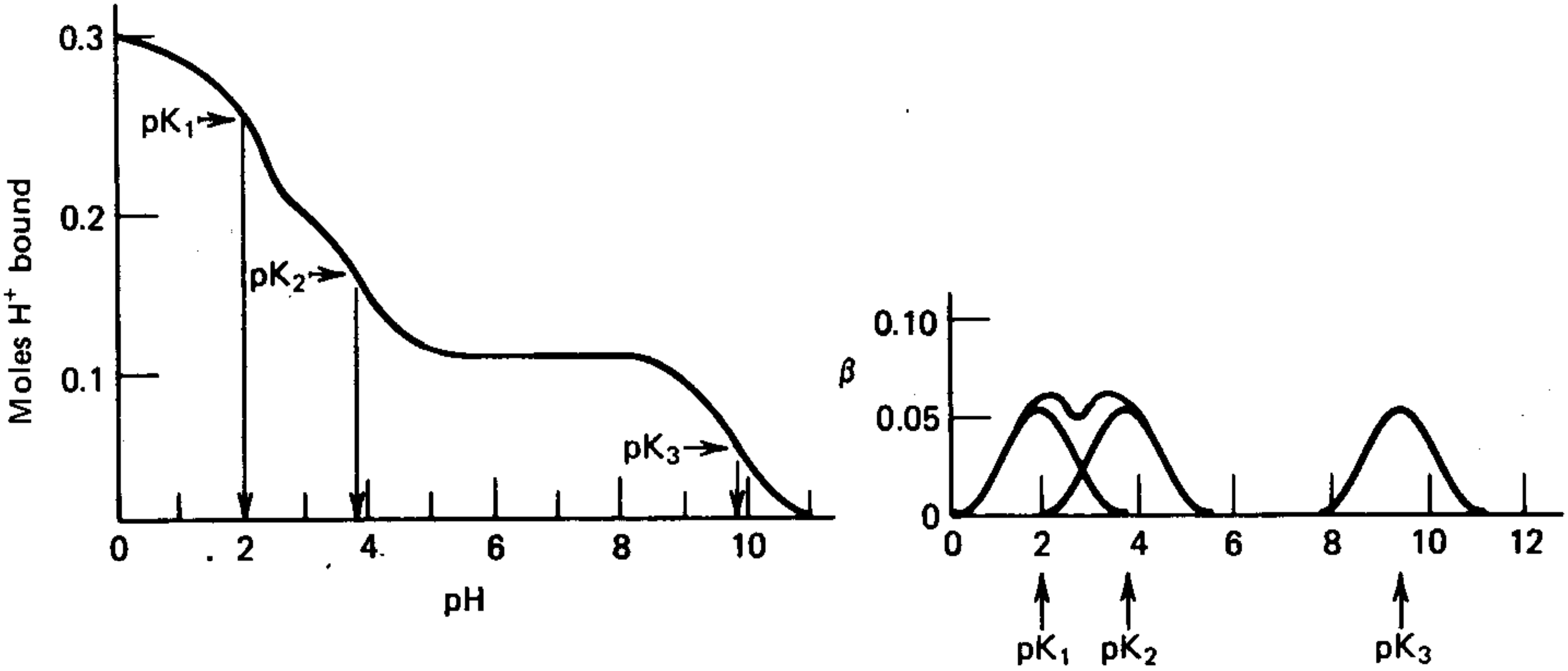


FIG. 4–8. Buffer index of 0.10 molar acetic acid as a function of pH. The minima correspond to pure acetic acid and sodium acetate, the maximum to the equimolar mixture of the two.



(*a*) (*b*)

$$\boxed{\beta = \sum_i \frac{2.303\, K_i\, [\mathrm{H}^+]\; n_i [\mathrm{HA}]_0}{(K_i + [\mathrm{H}^+])^2}}$$

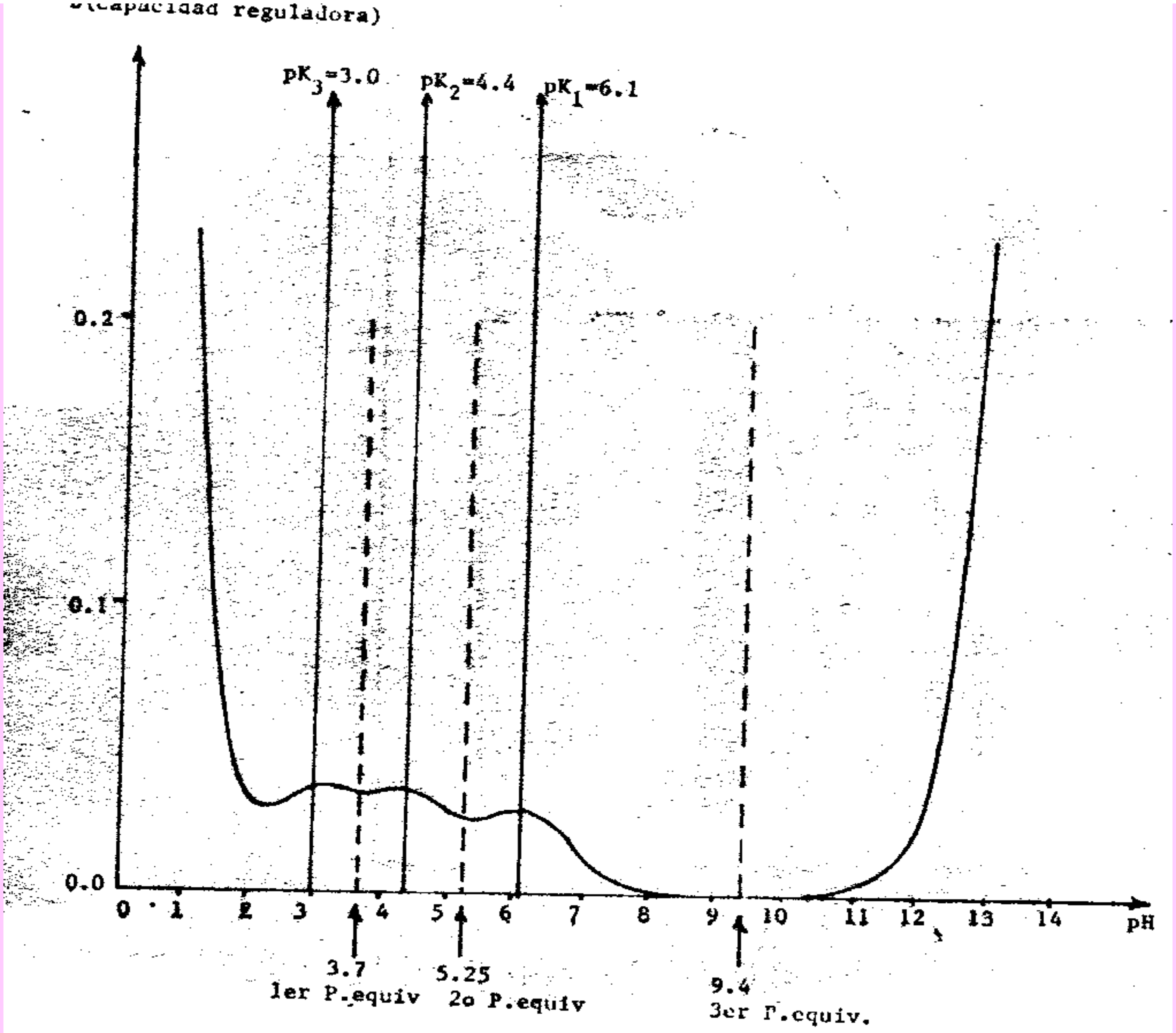


DIAGRAMA I.8. Capacidad reguladora de una disolución de ácido cítrico 0.0504 M en función del pH.

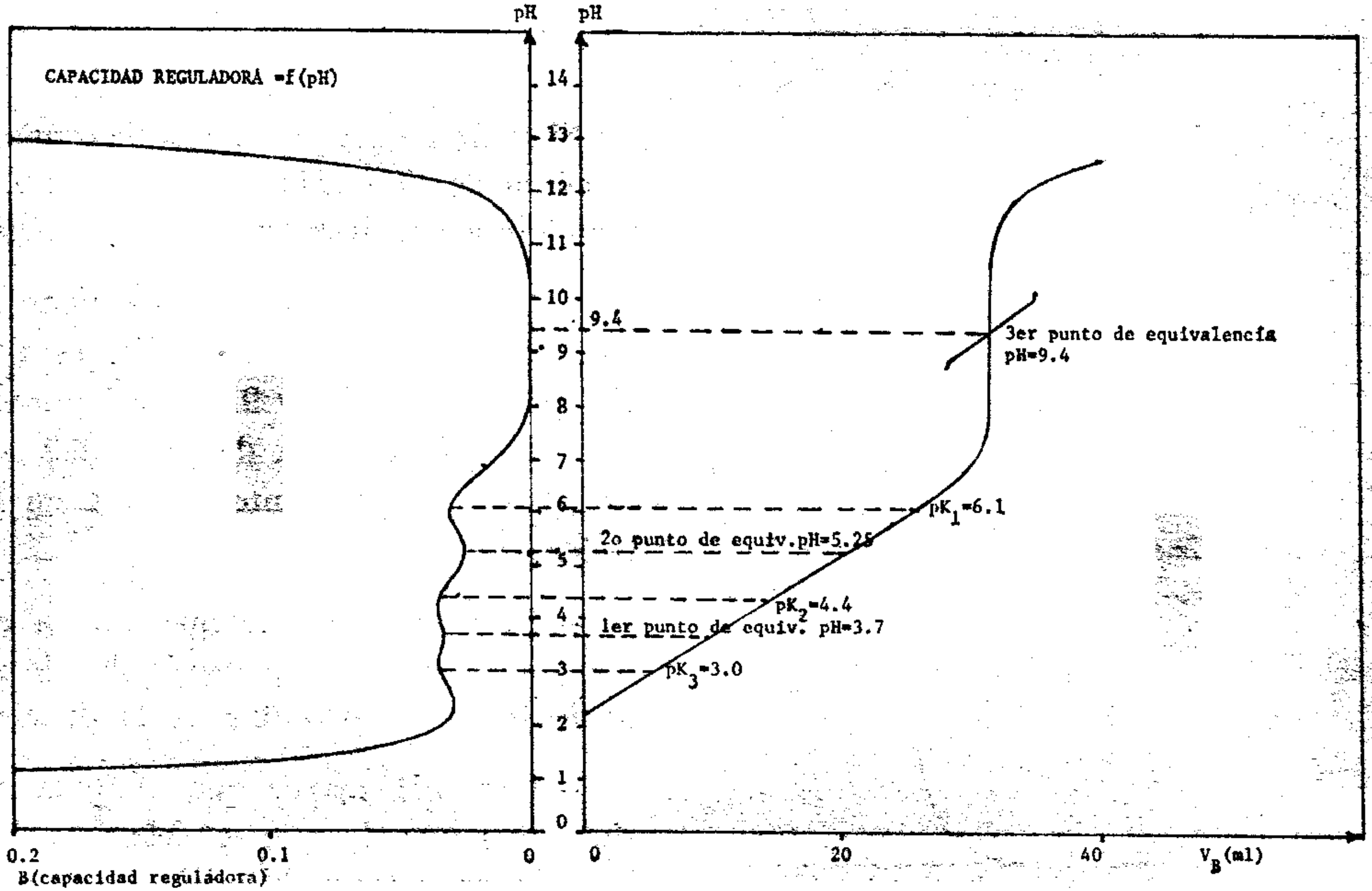


DIAGRAMA I.10. Curva teórica de titulación de 20 ml. de ácido cítrico 0.0504 M con NaOH 0.09 $pH = f(V_b)$. Se tomó en cuenta la dilución.

7.8 VALIDITY OF THE HENDERSON-HASSELBALCH EQUATION

Although equation (7-42) can easily be solved, it is not very informative; it is so complicated that looking at it gives us no insight into its meaning and validity. Fortunately, it is possible to put the equation into a more instructive form. Although the result [equation (7-46)] can be derived in a few steps by algebraic manipulation of (7-42) using $K_w = [H_3O^+][OH^-]$, it is useful to see how it can be derived from more fundamental considerations. We begin with the equilibrium expression

$$[H_3O^+] = K_a \frac{[HA]}{[A^-]} \tag{7-23}$$

take logarithms of both sides and multiply by −1; the result is

$$pH = pK_a + \log \frac{[A^-]}{[HA]} \tag{7-43}$$

[Note that this is *not* the same as equation (7-30), which deals with the *initial* concentrations of salt and acid.] Equation (7-36) can be rewritten as

$$[A^-] = C_s + [H_3O^+] - [OH^-] \tag{7-44}$$

---

[4] If the salt of a divalent cation [e.g., $Mg(NO_2)_2$] is used rather than a sodium salt, the factor C_s in equation (7-42) must be multiplied by 2.

and (7-33) can be rewritten as

$$[\mathrm{HA}] = C_a + C_s - [\mathrm{A}^-] \tag{7-45}$$

When we combine (7-43) and (7-44) with (7-45), the result is

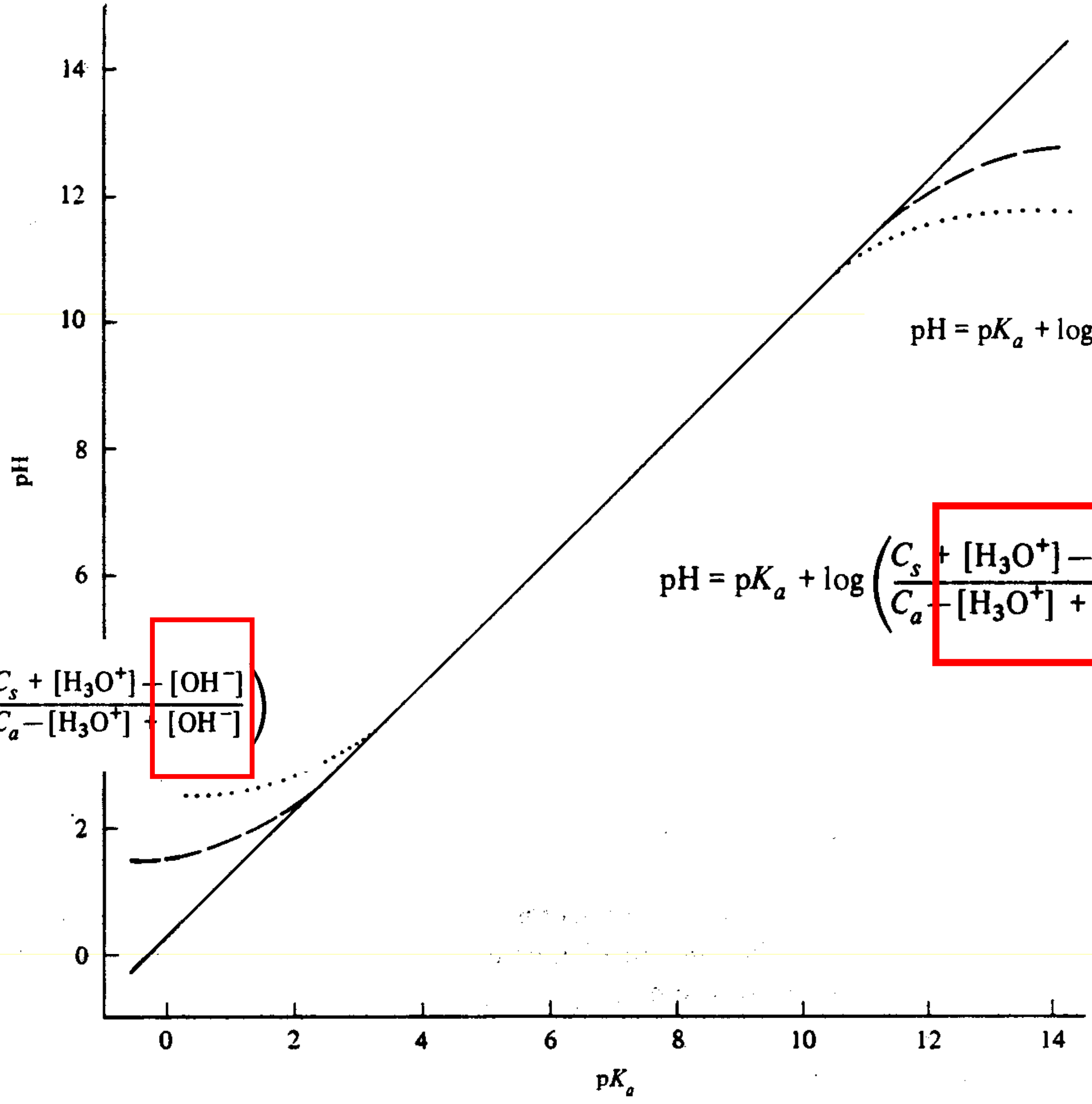
$$\mathrm{pH} = \mathrm{p}K_a + \log\left(\frac{C_s + [\mathrm{H_3O^+}] - [\mathrm{OH^-}]}{C_a - [\mathrm{H_3O^+}] + [\mathrm{OH^-}]}\right) \tag{7-46}$$

If the initial concentrations of salt and acid are significantly greater than both $[\mathrm{H_3O^+}]$ and $[\mathrm{OH^-}]$, then

$$C_s + [\mathrm{H_3O^+}] - [\mathrm{OH^-}] \approx C_s$$

$$C_a - [\mathrm{H_3O^+}] + [\mathrm{OH^-}] \approx C_a$$

and equation (7-46) becomes identical with the approximate form, the Henderson-Hasselbalch equation. Both $[\mathrm{H_3O^+}]$ and $[\mathrm{OH^-}]$ will be less than 0.001 *M* when the pH is in the range 3 to 11; C_a and C_s are rarely less than 0.1 *M* in practical buffers. Therefore, the Henderson-Hasselbalch equation may be used with confidence when the pH is between 3 and 11.

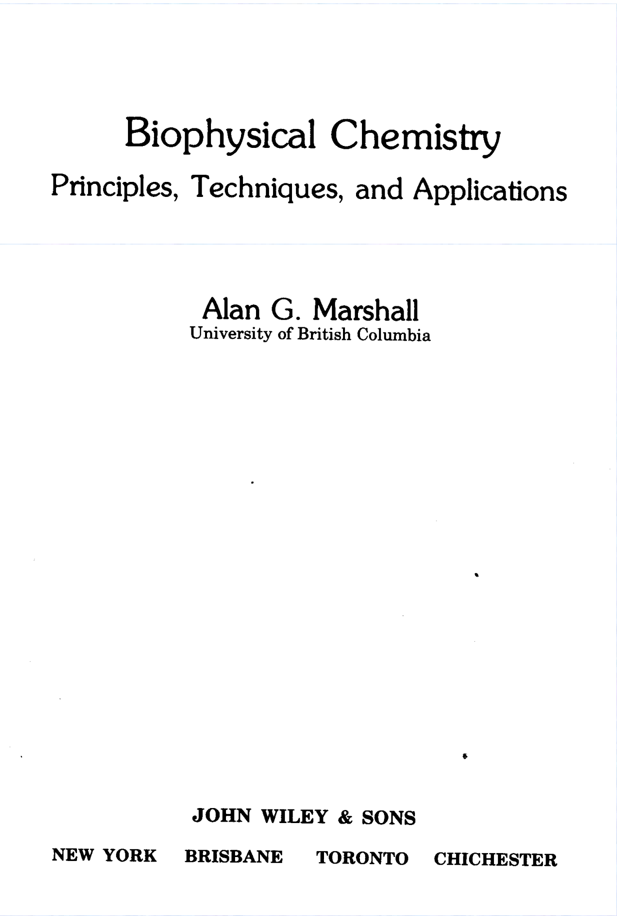


$$pH = pK_a + \log\left(\frac{C_s + \boxed{[H_3O^+]} - [OH^-]}{C_a - \boxed{[H_3O^+]} + [OH^-]}\right)$$

$$pH = pK_a + \log\left(\frac{C_s \boxed{+ [H_3O^+] - [OH^-]}}{C_a \boxed{- [H_3O^+] + [OH^-]}}\right)$$

$$pH = pK_a + \log\left(\frac{C_s + [H_3O^+] \boxed{- [OH^-]}}{C_a - [H_3O^+] \boxed{+ [OH^-]}}\right)$$

Figure 7.1 pH of a 2:1 (C_s:C_a) buffer as a function of acid strength (pK_a). Solid line, Henderson-Hasselbalch equation; dashed line, exact calculation for $C_s + C_a = 0.1\ M$; dotted line, exact calculation for $C_s + C_a = 0.01\ M$.



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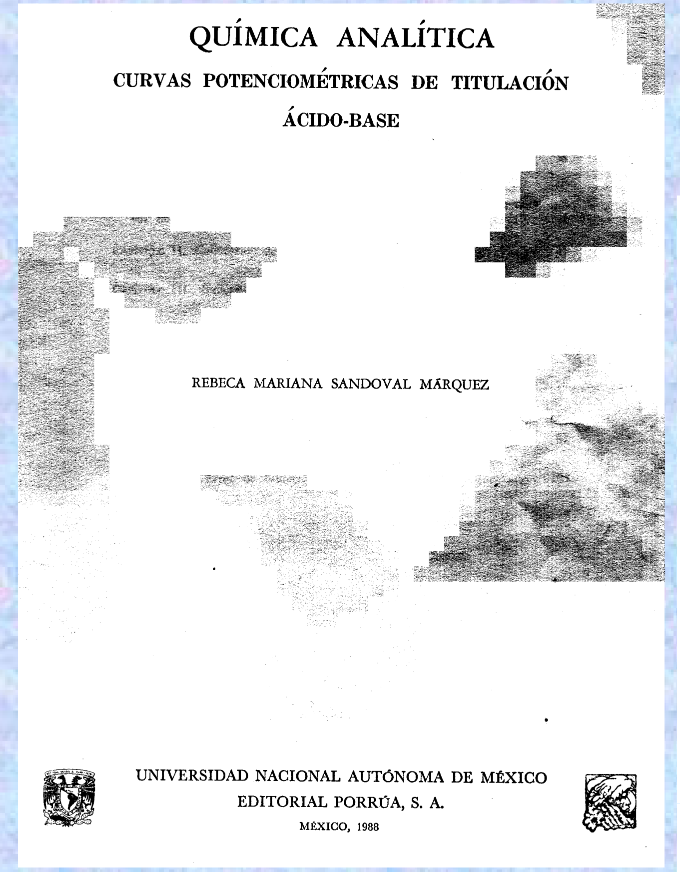

QUÍMICA ANALÍTICA

CURVAS POTENCIOMÉTRICAS DE TITULACIÓN ÁCIDO-BASE

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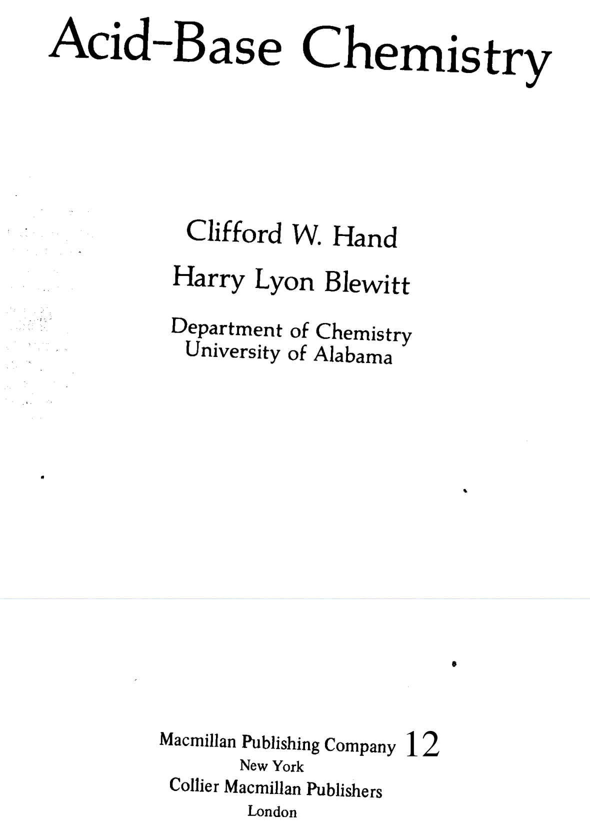

Acid-Base Chemistry

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