Supplementary Information

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Chapter 1

Derivation of α, β and γ

The condition of charge neutrality is:

$$[A_{\text{eff}}] + [H^+] \quad = \quad [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] \tag{1.1}$$

where,

$$[A_{\text{eff}}] \quad \equiv \quad [NH_4^+] - [NH_2COO^-] + [A_{\text{res}}] \tag{1.2}$$

On the other hand, the mass conservation of nitrogen demands:

$$[N] \quad = \quad [RNHCOOH] + [RNHCOO^-] + [NH_3] + [NH_4^+] \tag{1.3}$$

Substituting the mass action laws into Eq.(1.3) yields:

$$[N] \quad = \quad \frac{[NH_4^+][OH^-]}{K_b}K_X[CO_2] + K_X K_Y[CO_2]\frac{[NH_4^+][OH^-]^2}{K_b} + \frac{[NH_4^+][OH^-]}{K_b} + [NH_4^+] \tag{1.4}$$

$$= \quad \frac{[NH_4^+]}{K_b}\left(K_b + [OH^-] + [OH^-]K_X[CO_2] + K_X K_Y[CO_2][OH^-]^2\right) \tag{1.5}$$

Therefore, once $[OH^-]$ and P_{CO_2} (or $[CO_2]$) are given, $[NH_4^+]$ can be calculated as:

$$[NH_4^+] \quad = \quad \frac{K_b[N]}{K_b + [OH^-] + [OH^-]K_X[CO_2] + K_X K_Y[CO_2][OH^-]^2} \tag{1.6}$$

$[NH_3]$, $[RNHCOOH]$ and $[RNHCOO^-]$ can be calculated subsequently as:

$$[NH_3] \quad = \quad [NH_4^+] \times \frac{[OH^-]}{K_b} \tag{1.7}$$

$$[RNHCOOH] \quad = \quad [NH_3] \times K_X[CO_2] \tag{1.8}$$

$$[RNHCOO^-] \quad = \quad [RNHCOOH] \times K_Y[OH^-] \tag{1.9}$$

Once $[OH^-]$ and P_{CO_2} (or $[CO_2]$) are given, $[HCO_3^-]$ and $[CO_3^{2-}]$ can be subsequently calculated as:

$$[\text{HCO}_3^-] \quad = \quad K_1[\text{CO}_2][\text{OH}^-] \tag{1.10}$$
$$[\text{CO}_3^{2-}] \quad = \quad [\text{HCO}_3^-] \times K_2[\text{OH}^-] \tag{1.11}$$

Substituting the mass action laws and Eq.(1.6) into Eq.(1.1) yields:

$$[\text{H}^+] + [\text{A}_{\text{res}}] + \frac{[\text{N}](K_b - K_X K_Y [\text{CO}_2][\text{OH}^-]^2)}{K_b + [\text{OH}^-] + [\text{CO}_2](K_X[\text{OH}^-] + K_X K_Y[\text{OH}^-]^2)}$$
$$= \quad [\text{CO}_2](K_1[\text{OH}^-] + 2K_1 K_2[\text{OH}^-]^2) + [\text{OH}^-] \tag{1.12}$$

Since $[\text{H}^+]$ is negligible in our area of interest, Eq.(1.12) simplifies to:

$$[\text{A}_{\text{res}}] + \frac{[\text{N}](K_b - K_X K_Y [\text{CO}_2][\text{OH}^-]^2)}{K_b + [\text{OH}^-] + [\text{CO}_2](K_X[\text{OH}^-] + K_X K_Y[\text{OH}^-]^2)}$$
$$= \quad [\text{CO}_2](K_1[\text{OH}^-] + 2K_1 K_2[\text{OH}^-]^2) + [\text{OH}^-] \tag{1.13}$$

Eq.(1.13) is a quadratic equation for $[\text{CO}_2]$ and thus $[\text{CO}_2]$ can be explicitly expressed as function of only one variable, $[\text{OH}^-]$, as:

$$[\text{CO}_2] = f([\text{OH}^-]) \quad \equiv \quad \frac{-\beta + \sqrt{\beta^2 - 4\alpha\gamma}}{2\alpha} \tag{1.14}$$
$$= \quad \frac{\beta}{2\alpha}\left(\sqrt{1 - \frac{4\alpha\gamma}{\beta^2}} - 1\right) \tag{1.15}$$

where,

$$\alpha \quad = \quad (K_X[\text{OH}^-] + K_X K_Y[\text{OH}^-]^2)(K_1[\text{OH}^-] + 2K_1 K_2[\text{OH}^-]^2) \tag{1.16}$$
$$= \quad [\text{OH}^-]^4 2 K_X K_Y K_1 K_2$$
$$+ [\text{OH}^-]^3 K_X K_1 (K_Y + 2K_2)$$
$$+ [\text{OH}^-]^2 K_X K_1$$
$$\tag{1.17}$$

$$\beta \quad = \quad (K_b + [\text{OH}^-])(K_1[\text{OH}^-] + 2K_1 K_2[\text{OH}^-]^2)$$
$$+ [\text{OH}^-](K_X[\text{OH}^-] + K_X K_Y[\text{OH}^-]^2)$$
$$+ K_X K_Y[\text{OH}^-]^2[\text{N}]$$
$$- K_X[\text{OH}^-][\text{A}_{\text{res}}] - K_X K_Y[\text{OH}^-]^2[\text{A}_{\text{res}}]$$
$$\tag{1.18}$$

$$= \quad [\text{OH}^-]^3 (2K_1 K_2 + K_X K_Y)$$
$$+ [\text{OH}^-]^2 (K_1 + 2K_b K_1 K_2 + K_X + K_X K_Y([\text{N}] - [\text{A}_{\text{res}}]))$$
$$+ [\text{OH}^-](K_b K_1 - K_X[\text{A}_{\text{res}}])$$
$$\tag{1.19}$$

$$\gamma \quad = \quad [\text{OH}^-]^2 + [\text{OH}^-](K_b - [\text{A}_{\text{res}}]) - K_b([\text{N}] + [\text{A}_{\text{res}}]) \tag{1.20}$$

If we assume $[\text{A}_{\text{residual}}] = 0$, β and γ simplify to:

$$
\begin{aligned}
\beta \quad = \quad & (K_b + [\text{OH}^-])(K_1[\text{OH}^-] + 2K_1K_2[\text{OH}^-]^2) \\
& +[\text{OH}^-](K_X[\text{OH}^-] + K_X K_Y[\text{OH}^-]^2) \\
& +K_X K_Y[\text{OH}^-]^2[\text{N}]
\end{aligned}
\tag{1.21}
$$

$$
\begin{aligned}
= \quad & [\text{OH}^-]^3(2K_1K_2 + K_X K_Y) \\
& +[\text{OH}^-]^2(K_1 + 2K_bK_1K_2 + K_X + K_X K_Y[\text{N}]) \\
& +[\text{OH}^-]K_bK_1
\end{aligned}
\tag{1.22}
$$

$$
\gamma \quad = \quad [\text{OH}^-]^2 + K_b[\text{OH}^-] - K_b[\text{N}]
\tag{1.23}
$$

Note that the other root of Eq.(1.13) always takes a negative value and thus does not make physical sense.

$[\text{CO}_2]$ becomes zero when $\gamma = 0$, in other words, when the $[\text{OH}^-]_{\text{max}}$ satisfies the following equation:

$$
[\text{OH}^-]_{\text{max}}^2 + K_b[\text{OH}^-]_{\text{max}} - K_b[\text{N}] \quad = \quad 0
\tag{1.24}
$$

or,

$$
[\text{OH}^-]_{\text{max}} \quad = \quad \frac{K_b}{2}\left(\sqrt{1 + \frac{4[\text{N}]}{K_b}} - 1\right)
\tag{1.25}
$$

If $[\text{OH}^-]$ exceeds $[\text{OH}^-]_{\text{max}}$, it results in $[\text{CO}_2] < 0$. Since $[\text{CO}_2]$ needs to be positive, $[\text{OH}^-]_{\text{max}}$ set the maximum pH of this system.

Conversely, $[\text{OH}^-]$ can be implicitly expressed as function of only one variable, $[\text{CO}_2]$, as:

$$
[\text{OH}^-] \quad = \quad f^{-1}([\text{CO}_2])
\tag{1.26}
$$

By substituting Eq.(1.26) into Eq.(1.6), $[\text{NH}_4^+]$ can be implicitly expressed as function of only one variable, $[\text{CO}_2]$, as:

$$
[\text{NH}_4^+] \quad = \quad \frac{K_b[\text{N}]}{K_b + f^{-1}([\text{CO}_2]) + f^{-1}([\text{CO}_2])K_X[\text{CO}_2] + K_X K_Y[\text{CO}_2](f^{-1}([\text{CO}_2])^2}
\tag{1.27}
$$

$$
\equiv \quad g([\text{CO}_2])
\tag{1.28}
$$

Therefore, the effective alkalinity $[\text{A}_{\text{eff}}]$, can be expressed as:

$$
[\text{A}_{\text{eff}}] \quad = \quad g([\text{CO}_2]) \times \left(1 - \frac{K_X K_Y}{K_b}[\text{CO}_2]\left\{f^{-1}([\text{CO}_2])\right\}^2\right)
\tag{1.29}
$$

The CO_2 loading status θ can be defined as:

$$
\theta \quad \equiv \quad \theta_{\text{DOC}} + \theta_{\text{DIC}}
\tag{1.30}
$$

3

where,

$$\theta_{\text{DOC}} \equiv \frac{[\text{DOC}]}{[\text{N}]} \tag{1.31}$$

$$\theta_{\text{DIC}} \equiv \frac{[\text{DIC}]}{[\text{N}]} \tag{1.32}$$

Note that DOC and DIC represent Dissolved Organic Carbon and Dissolved Inorganic Carbon, respectively, which are defined as:

$$[\text{DOC}] \equiv [\text{NH}_2\text{COOH}] + [\text{NH}_2\text{COO}^-] \tag{1.33}$$
$$[\text{DIC}] \equiv [\text{CO}_2] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] \tag{1.34}$$

Therefore,

$$\begin{aligned}
\theta &= \frac{K_X}{K_b[\text{N}]} g([\text{CO}_2])[\text{CO}_2] f^{-1}([\text{CO}_2]) \left(1 + K_Y f^{-1}([\text{CO}_2]) \right) \\
&\quad + \frac{[\text{CO}_2]}{[\text{N}]} \left(1 + K_1 f^{-1}([\text{CO}_2]) + K_1 K_2 \left\{ f^{-1}([\text{CO}_2]) \right\}^2 \right)
\end{aligned} \tag{1.35}$$

Chapter 2

Small $[OH^-]$ limit

In this limit of $[CO_2] \to \infty$ (in other words, in the limit of $[OH^-] \to 0$),

$$
\begin{aligned}
\alpha &= K_1 K_X [OH^-]^2 + o([OH^-]^2) \quad \text{as } [OH^-] \to 0 & (2.1) \\
\beta &= K_b K_1 [OH^-] + o([OH^-]) \quad \text{as } [OH^-] \to 0 & (2.2) \\
\gamma &= -K_b [N] + o(1) \quad \text{as } [OH^-] \to 0 & (2.3) \\
& & (2.4)
\end{aligned}
$$

Therefore,

$$
\frac{\beta}{2\alpha} = \frac{K_b + o(1)}{2 K_X [OH^-] + o([OH^-])} \quad \text{as } [OH^-] \to 0 \tag{2.5}
$$

$$
\frac{4\alpha\gamma}{\beta^2} = -\frac{4 K_X [N]}{K_b K_1} + o(1) \quad \text{as } [OH^-] \to 0 \tag{2.6}
$$

$$
(2.7)
$$

Note that the o-notation is used to indicate the order of a function and to describe the asymptotic behavior of a function. Assuming $\phi(x) \neq 0$ for all $x \neq a$ in some interval containing a, the notation

$$
\psi(x) = o(\phi(x)) \quad \text{as } x \to a \tag{2.8}
$$

means that

$$
\lim_{x \to a} \frac{\psi(x)}{\phi(x)} = 0 \tag{2.9}
$$

Substituting Eq.(2.5) and Eq.(2.6) into Eq.(1.15) yields:

$$
[CO_2] \sim \frac{K_b}{2 K_X [OH^-]} \left(\sqrt{1 + \frac{4 K_X [N]}{K_b K_1}} - 1 \right) \tag{2.10}
$$

$$
(2.11)
$$

Substituting Eq.(2.10) into Eq.(1.6) yields

$$[\text{NH}_4^+] \quad \sim \quad \frac{2[\text{N}]}{\sqrt{1 + \frac{4K_X[\text{N}]}{K_b K_1}} + 1} \tag{2.12}$$

$$= \quad \frac{K_b K_1}{2K_X} \left(\sqrt{1 + \frac{4K_X[\text{N}]}{K_b K_1}} - 1 \right) \tag{2.13}$$

Therefore, the effective alkalinity in this limit is

$$[\text{A}_{\text{eff}}] \quad = \quad [\text{NH}_4^+](1 - \frac{K_X K_Y}{K_b}[\text{CO}_2][\text{OH}^-]^2) \tag{2.14}$$

$$\sim \quad [\text{NH}_4^+] \tag{2.15}$$

$$\sim \quad \frac{2[\text{N}]}{\sqrt{1 + \frac{4K_X[\text{N}]}{K_b K_1}} + 1} \tag{2.16}$$

$$= \quad \frac{K_b K_1}{2K_X} \left(\sqrt{1 + \frac{4K_X[\text{N}]}{K_b K_1}} - 1 \right) \tag{2.17}$$

[NH$_2$COOH] in this limit is

$$[\text{NH}_2\text{COOH}] \quad = \quad K_X[\text{CO}_2]\frac{[\text{NH}_4^+][\text{OH}^-]}{K_b} \tag{2.18}$$

$$\sim \quad \cancel{K_X}\frac{\cancel{K_b}}{2\cancel{K_X}\cancel{[\text{OH}^-]}} \left(\sqrt{1 + \frac{4K_X[\text{N}]}{K_b K_1}} - 1 \right) \frac{[\text{NH}_4^+]\cancel{[\text{OH}^-]}}{\cancel{K_b}} \tag{2.19}$$

$$= \quad \frac{[\text{NH}_4^+]}{2} \left(\sqrt{1 + \frac{4K_X[\text{N}]}{K_b K_1}} - 1 \right) \tag{2.20}$$

$$= \quad [\text{N}]\frac{\left(\sqrt{1 + \frac{4K_X[\text{N}]}{K_b K_1}} - 1 \right)}{\left(\sqrt{1 + \frac{4K_X[\text{N}]}{K_b K_1}} + 1 \right)} \tag{2.21}$$

$$= \quad \frac{K_b K_1}{4K_X} \left(\sqrt{1 + \frac{4K_X[\text{N}]}{K_b K_1}} - 1 \right)^2 \tag{2.22}$$

[NH$_2$COO$^-$] in this limit is

$$[\text{NH}_2\text{COO}^-] \quad = \quad K_Y[\text{OH}^-][\text{NH}_2\text{COOH}] \tag{2.23}$$

$$\sim \quad \frac{K_b K_1 K_Y[\text{OH}^-]}{4K_X} \left(\sqrt{1 + \frac{4K_X[\text{N}]}{K_b K_1}} - 1 \right)^2 \tag{2.24}$$

Therefore, θ_{DOC} in this limit is

6

$$\theta_{\text{DOC}} \quad \sim \quad \frac{[\text{NH}_2\text{COOH}]}{[\text{N}]} \tag{2.25}$$

$$\sim \quad \frac{\left(\sqrt{1+\frac{4K_X[\text{N}]}{K_bK_1}}-1\right)}{\left(\sqrt{1+\frac{4K_X[\text{N}]}{K_bK_1}}+1\right)} \tag{2.26}$$

$$= \quad \frac{K_bK_1}{4K_X[\text{N}]}\left(\sqrt{1+\frac{4K_X[\text{N}]}{K_bK_1}}-1\right)^2 \tag{2.27}$$

$[\text{NH}_3]$ in this limit is

$$[\text{NH}_3] \quad = \quad \frac{[\text{NH}_4^+][\text{OH}^-]}{K_b} \tag{2.28}$$

$$\sim \quad \frac{[\text{OH}^-]}{\cancel{K_b}}\frac{\cancel{K_b}K_1}{2K_X}\left(\sqrt{1+\frac{4K_X[\text{N}]}{K_bK_1}}-1\right) \tag{2.29}$$

$$= \quad \frac{K_1[\text{OH}^-]}{2K_X}\left(\sqrt{1+\frac{4K_X[\text{N}]}{K_bK_1}}-1\right) \tag{2.30}$$

$[\text{HCO}_3^-]$ in this limit is

$$[\text{HCO}_3^-] \quad = \quad K_1[\text{OH}^-][\text{CO}_2] \tag{2.31}$$

$$\sim \quad K_1\cancel{[\text{OH}^-]}\frac{K_b}{2K_X\cancel{[\text{OH}^-]}}\left(\sqrt{1+\frac{4K_X[\text{N}]}{K_bK_1}}-1\right) \tag{2.32}$$

$$= \quad \frac{K_bK_1}{2K_X}\left(\sqrt{1+\frac{4K_X[\text{N}]}{K_bK_1}}-1\right) \tag{2.33}$$

$$\sim \quad [\text{NH}_4^+] \tag{2.34}$$

$[\text{CO}_3^{2-}]$ in this limit is

$$[\text{CO}_3^{2-}] \quad = \quad K_2[\text{OH}^-][\text{HCO}_3^-] \tag{2.35}$$

$$\sim \quad \frac{K_bK_1K_2[\text{OH}^-]}{2K_X}\left(\sqrt{1+\frac{4K_X[\text{N}]}{K_bK_1}}-1\right) \tag{2.36}$$

Therefore,

$$\theta_{\text{DICI}} \quad \sim \quad \frac{[\text{HCO}_3^-]}{[\text{N}]} \tag{2.37}$$

$$\sim \quad \frac{K_bK_1}{2K_X[\text{N}]}\left(\sqrt{1+\frac{4K_X[\text{N}]}{K_bK_1}}-1\right) \tag{2.38}$$

One can confirm that $\theta_{\text{DICI}} + \theta_{\text{DOC}} = 1$ is satisfied in this limit as follows:

$$\theta_{\text{DICI}} + \theta_{\text{DOC}} \sim \frac{K_b K_1}{4K_X[\text{N}]} \left(\sqrt{1 + \frac{4K_X[\text{N}]}{K_b K_1}} - 1 \right) \tag{2.39}$$

$$\times \left(\sqrt{1 + \frac{4K_X[\text{N}]}{K_b K_1}} - 1 + 2 \right) \tag{2.40}$$

$$= \frac{\cancel{K_b K_1}}{\cancel{4K_X[\text{N}]}} \frac{\cancel{4K_X[\text{N}]}}{\cancel{K_b K_1}} \tag{2.41}$$

$$= 1 \tag{2.42}$$

These mean that this model reduces to the isotherm model of alkaline aqueous solutions in a hydroxide-carbonate-bicarbonate system with a constant alkalinity of [N].

Chapter 3

Physical large $[OH^-]$ limit

Mathematically, we can take the limit of $[OH^-] \to \infty$. However, $[CO_2]$ turns negative when $[OH^-]$ is larger than a certain value, $[OH^-]_{max}$, which is defined as:

$$[OH^-]_{max} = \frac{K_b}{2}\left(\sqrt{1 + \frac{4[N]}{K_b}} - 1\right) \tag{3.1}$$

Therefore, the upper bound of $[OH^-]$ is given by $[OH^-]_{max}$. In this limit, $\gamma = 0$ and thus:

$$\sqrt{1 - \frac{4\alpha\gamma}{\beta^2}} - 1 \sim 0 \tag{3.2}$$

Regarding $\frac{\beta}{2\alpha}$, we can just substitute $[OH^-] = [OH^-]_{max}$ into $\frac{\beta}{2\alpha}$ to obtain $\frac{\beta}{2\alpha}$ in this limit. In case that $[OH^-]_{max}$ is large enough to allow us to take only the leading terms, we obtain:

$$\frac{\beta}{2\alpha} \sim \frac{2K_1K_2 + K_XK_Y}{4[OH^-]_{max}K_XK_YK_1K_2} \tag{3.3}$$

In any case, $\frac{\beta}{2\alpha}$ is a constant value. Hence,

$$[CO_2] = \frac{\beta}{2\alpha}\left(\sqrt{1 - \frac{4\alpha\gamma}{\beta^2}} - 1\right) \tag{3.4}$$

$$\sim 0 \tag{3.5}$$

Therefore,

$$[NH_4^+] = \frac{K_b[N]}{K_b + [OH^-] + [OH^-]K_X[CO_2] + K_XK_Y[CO_2][OH^-]^2} \tag{3.6}$$

$$\sim \frac{K_b[N]}{K_b + [OH^-]_{max} + \underbrace{[OH^-]_{max}K_X \cdot 0 + K_XK_Y \cdot 0 \cdot [OH^-]_{max}^2}_{\to 0}} \tag{3.7}$$

$$\sim \frac{K_b[N]}{K_b + [OH^-]_{max}} \tag{3.8}$$

$$= [OH^-]_{max} \tag{3.9}$$

$$[\text{NH}_3] = \frac{[\text{NH}_4^+][\text{OH}^-]}{K_b} \tag{3.10}$$

$$\sim \frac{[\text{OH}^-]_{\text{max}}^2}{K_b} \tag{3.11}$$

$$[\text{NH}_2\text{COOH}] = K_X[\text{NH}_3][\text{CO}_2] \tag{3.12}$$

$$\sim K_X\frac{[\text{OH}^-]_{\text{max}}^2}{K_b} \cdot 0 \tag{3.13}$$

$$= 0 \tag{3.14}$$

$$[\text{NH}_2\text{COO}^-] = K_Y[\text{NH}_2\text{COOH}][\text{OH}^-] \tag{3.15}$$

$$\sim K_Y \cdot 0 \cdot [\text{OH}^-]_{\text{max}} \tag{3.16}$$

$$= 0 \tag{3.17}$$

The effective alkalinity in this limit is

$$[\text{A}_{\text{eff}}] \sim \frac{[\text{NH}_4^+]}{[\text{N}]} \tag{3.18}$$

$$\sim \frac{K_b[\text{N}]}{K_b + [\text{OH}^-]_{\text{max}}} \tag{3.19}$$

$$= [\text{OH}^-]_{\text{max}} \tag{3.20}$$

Also,

$$[\text{HCO}_3^-] = K_1[\text{OH}^-][\text{CO}_2] \tag{3.21}$$

$$\sim K_1[\text{OH}^-]_{\text{max}} \cdot 0 \tag{3.22}$$

$$= 0 \tag{3.23}$$

$$[\text{CO}_3^{2-}] = K_2[\text{OH}^-][\text{HCO}_3^-] \tag{3.24}$$

$$\sim K_2[\text{OH}^-]_{\text{max}} \cdot 0 \tag{3.25}$$

$$= 0 \tag{3.26}$$

$$\theta_{\text{DICI}} = \frac{[\text{HCO}_3^-] + [\text{CO}_3^{2-}]}{[\text{N}]} \tag{3.27}$$

$$\sim 0 \tag{3.28}$$

$$\theta_{\text{DOC}} = \frac{[\text{NH}_2\text{COO}^-] + [\text{NH}_2\text{COOH}]}{[\text{N}]} \tag{3.29}$$

$$\sim 0 \tag{3.30}$$

$$\theta \sim 0 \tag{3.31}$$

10

Chapter 4

Unphysical large $[\mathrm{OH}^-]$ limit

Even though the limit of $[\mathrm{OH}^-] \to \infty$ beyond $[\mathrm{OH}^-]_{\mathrm{max}}$ does not make any physical sense, investigating the asymptotic behavior in $[\mathrm{OH}^-] \to \infty$ is useful for better understanding of the mathematical structure of this system.

In this limit,

$$\frac{\beta}{2\alpha} \quad \sim \quad \frac{2K_1K_2 + K_XK_Y}{4K_XK_YK_1K_2} > 0 \tag{4.1}$$

$$\sqrt{1 - \frac{4\alpha\gamma}{\beta^2}} - 1 \quad \sim \quad \sqrt{1 - \frac{8K_XK_YK_1K_2}{(2K_1K_2 + K_XK_Y)^2}} - 1 < 0 \tag{4.2}$$

Therefore, $[\mathrm{CO}_2]$ takes an unphysical negative value in this limit as:

$$[\mathrm{CO}_2] \quad \sim \quad -\frac{\delta_2}{[\mathrm{OH}^-]} < 0 \tag{4.3}$$

where, a positive number δ_2 is defined for convenience as:

$$\delta_2 \quad \equiv \quad -\lim_{[\mathrm{OH}^-]\to\infty} [\mathrm{CO}_2][\mathrm{OH}^-] \tag{4.4}$$

$$= \quad -\frac{2K_1K_2 + K_XK_Y}{4K_XK_YK_1K_2}\left(\sqrt{1 - \frac{8K_XK_YK_1K_2}{(2K_1K_2 + K_XK_Y)^2}} - 1\right) \tag{4.5}$$

Hence,

$$[\mathrm{NH}_4^+] \quad = \quad \frac{K_b[\mathrm{N}]}{K_b + [\mathrm{OH}^-] + [\mathrm{OH}^-]K_X[\mathrm{CO}_2] + K_XK_Y[\mathrm{CO}_2][\mathrm{OH}^-]^2} \tag{4.6}$$

$$\sim \quad \frac{K_b[\mathrm{N}]}{[\mathrm{OH}^-](1 + K_XK_Y\underbrace{[\mathrm{CO}_2][\mathrm{OH}^-]}_{\to -\delta_2})} \tag{4.7}$$

$$\sim \quad \frac{K_b[\mathrm{N}]}{[\mathrm{OH}^-](1 - K_XK_Y\delta_2)} \tag{4.8}$$

11

$$[\text{NH}_3] \quad = \quad \frac{[\text{NH}_4^+][\text{OH}^-]}{K_b} \tag{4.9}$$

$$\sim \quad \frac{\cancel{[\text{OH}^-]}}{\cancel{K_b}} \frac{\cancel{K_b}[\text{N}]}{\cancel{[\text{OH}^-]}(1 - K_X K_Y \delta_2)} \tag{4.10}$$

$$= \quad \frac{[\text{N}]}{1 - K_X K_Y \delta_2} \tag{4.11}$$

$$[\text{NH}_2\text{COOH}] \quad = \quad K_X[\text{NH}_3][\text{CO}_2] \tag{4.12}$$

$$\sim \quad -\frac{K_X[\text{N}]\delta_2}{[\text{OH}^-](1 - K_X K_Y \delta_2)} \tag{4.13}$$

$$[\text{NH}_2\text{COO}^-] \quad = \quad K_Y[\text{NH}_2\text{COOH}][\text{OH}^-] \tag{4.14}$$

$$\sim \quad -K_Y \frac{K_X[\text{N}]}{1 - K_X K_Y \delta_2} \cdot \frac{\delta_2}{\cancel{[\text{OH}^-]}} \cdot \cancel{[\text{OH}^-]} \tag{4.15}$$

$$= \quad -\frac{K_X K_Y [\text{N}]\delta_2}{1 - K_X K_Y \delta_2} \tag{4.16}$$

$$[\text{A}_{\text{eff}}] \quad \sim \quad -[\text{NH}_2\text{COO}^-] \tag{4.17}$$

$$\sim \quad \frac{K_X K_Y [\text{N}]\delta_2}{1 - K_X K_Y \delta_2} \tag{4.18}$$

$$[\text{HCO}_3^-] \quad = \quad K_1 \underbrace{[\text{OH}^-][\text{CO}_2]}_{\to -\delta_2} \tag{4.19}$$

$$\sim \quad -\delta_2 K_1 \tag{4.20}$$

$$[\text{CO}_3^{2-}] \quad = \quad K_2[\text{OH}^-][\text{HCO}_3^-] \to -\infty < 0 \tag{4.21}$$

$$\sim \quad -K_1 K_2 [\text{OH}^-]\delta_2 \tag{4.22}$$

$$\theta_{\text{DICI}} \quad = \quad \frac{[\text{HCO}_3^-] + [\text{CO}_3^{2-}]}{[\text{N}]} \tag{4.23}$$

$$\sim \quad -\frac{K_1 K_2 [\text{OH}^-]\delta_2}{[\text{N}]} \to -\infty < 0 \tag{4.24}$$

$$\theta_{\text{DOC}} \quad = \quad \frac{[\text{NH}_2\text{COO}^-] + [\text{NH}_2\text{COOH}]}{[\text{N}]} \tag{4.25}$$

$$\sim \quad \frac{[\text{NH}_2\text{COO}^-]}{[\text{N}]} \tag{4.26}$$

$$\sim \quad -\frac{K_X K_Y \delta_2}{1 - K_X K_Y \delta_2} \tag{4.27}$$

$$\theta_{\text{DOC}} + \theta_{\text{DICI}} \quad \sim \quad -\frac{K_1 K_2 [\text{OH}^-]\delta_2}{[\text{N}]} \to -\infty < 0 \tag{4.28}$$

$$\theta \quad \sim \quad -\frac{K_1 K_2 [\text{OH}^-]\delta_2}{[\text{N}]} \to -\infty < 0 \tag{4.29}$$

Chapter 5

Comparison between the model and Pexton and Badger (1938) for [N]=1.5 mol L^{-1}

For [N]=1.5 mol L^{-1} and $T = 20°$C, Pexton and Badger (1938) provides two valid data points. Fig.(5.1) shows a comparison between the model and Pexton and Badger (1938) for [N]=1.5 mol L^{-1} and $T = 20°$C. $\gamma_{\pm}^{-2} = 4.0$ has been applied for the fitting of these data. Note that Pexton and Badger (1938) does not provide data points for [N]=1.5 mol L^{-1} and $T = 40°$C.
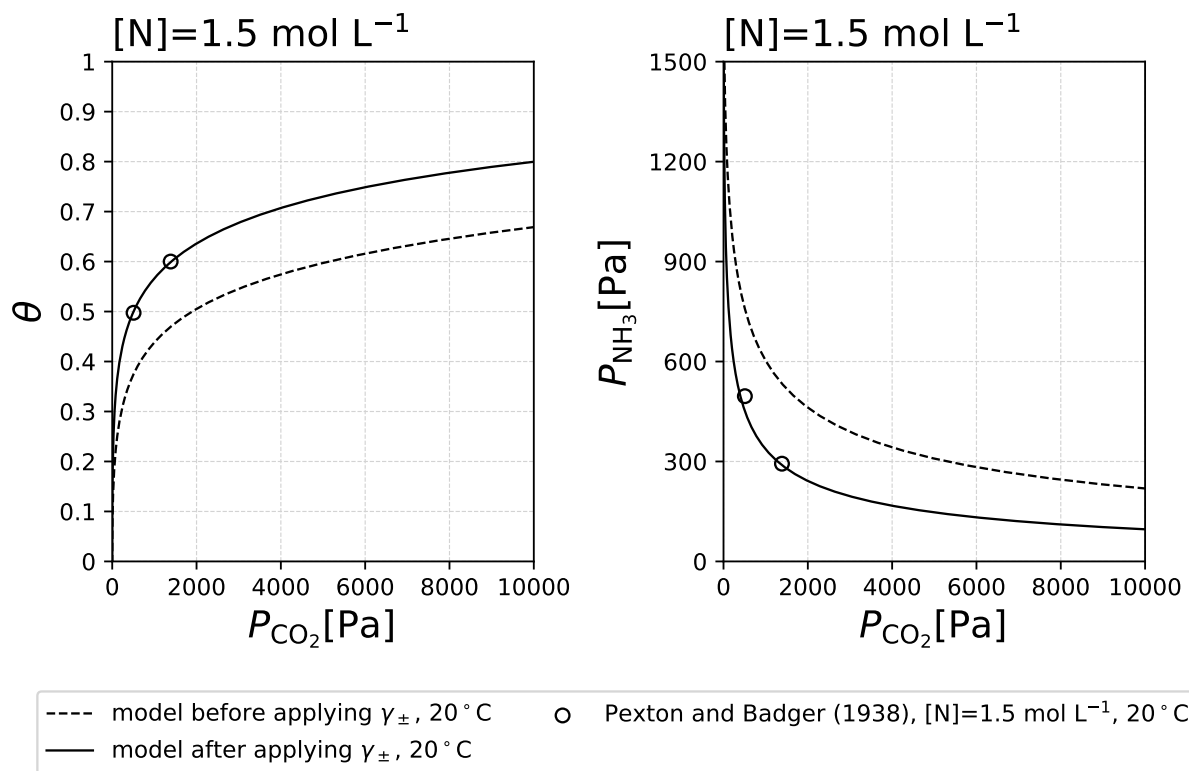
Figure 5.1: A comparison between the model and Pexton and Badger (1938) for [N]=1.5 mol L^{-1} and 20°C. The value of $\gamma_{\pm}^{-2}$ is 4.0.

Chapter 6

Comparison between the model and Pexton and Badger (1938) for 10-100000 Pa on a logarithmic scale

In the main text, the data falling between 0-10000 Pa are shown. There are a few points above 10000 Pa which have been used in fitting the data but could not be shown on an intuitive linear scale. In Fig.6.1 and Fig.6.2, we show all the data on a logarithmic scale that ranges from 10 to 100000 Pa.
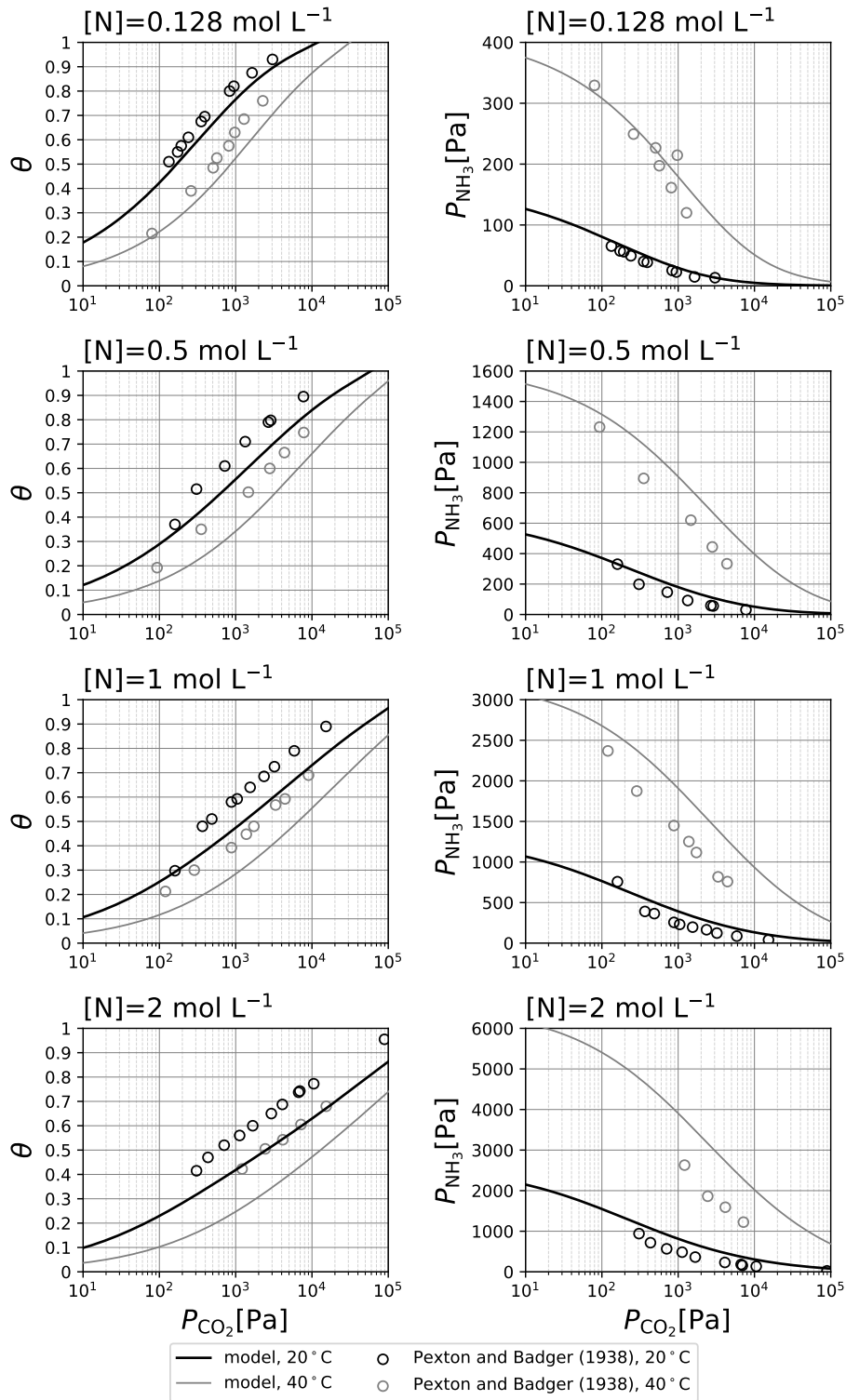
Figure 6.1: A comparison of the experimental data from Pexton and Badger (1938) and the model at $T = 20°C$ or $T = 40°C$ before influence of ionic strength is corrected.
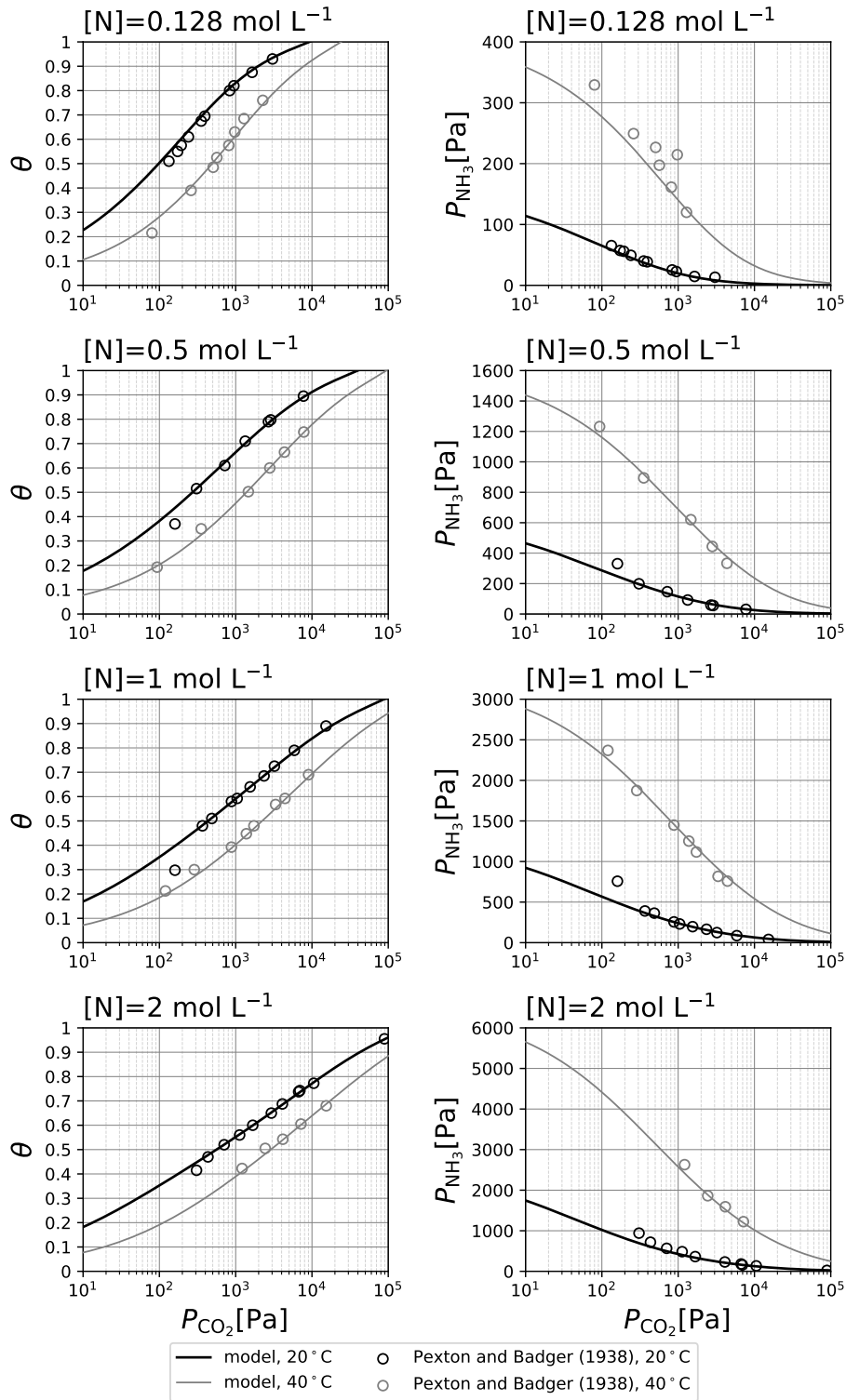
Figure 6.2: A comparison of the experimental data from Pexton and Badger (1938) and the model at $T = 20°$C or $T = 40°$C after $\gamma_\pm$ is applied to correct the influence of ionic strength.