

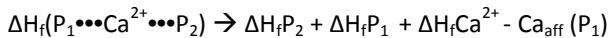
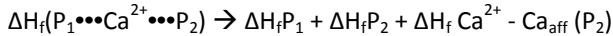
Supplementary Information

Derivation of equations (1) and (2)

For the process: $P + H^+ \rightarrow PH^+$, the proton affinity (PA) is defined as: $PA(P) = \Delta H_f(P) + \Delta H_f(H^+) - \Delta H_f(PH^+)$

Similarly, for the process: $P + Ca^{2+} \rightarrow (P \cdots Ca^{2+})$, the calcium affinity (Ca_{aff}) is: $Ca_{aff} = \Delta H_f(P) + \Delta H_f(Ca^{2+}) - \Delta H_f(P \cdots Ca^{2+})$

1. $P_1 \cdots Ca^{2+} \cdots P_2$ dissociating to $P_1 + (P_2 \cdots Ca^{2+})$ or to $P_2 + (P_1 \cdots Ca^{2+})$



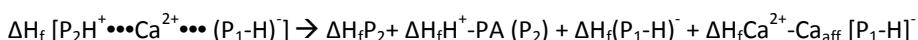
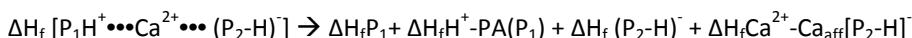
Subtract:

$$\Delta = \Delta Ca_{aff} (P)$$

2. $P_1 \cdots Ca^{2+} \cdots P_2$ dissociating to $P_1 H^+ + [(P_2 - H)^- \cdots Ca^{2+}]$ or to $P_2 H^+ + [(P_1 - H)^- \cdots Ca^{2+}]$



or



Subtract:

$$\Delta = \Delta H_f P_1 - \Delta H_f P_2 + \Delta H_f (P_2 - H)^- - \Delta H_f (P_1 - H)^- - PA(P_1) + PA(P_2) - Ca_{aff}[P_2 - H]^- + Ca_{aff}[P_1 - H]^-$$

$$\Delta = Ca_{aff}[P_1 - H] - Ca_{aff}[P_2 - H] - PA(P_1) - PA(P_2) + \Delta H_f P_1 - \Delta H_f P_2 + \Delta H_f [P_2 - H]^- - \Delta H_f [P_1 - H]^- \dots \dots \dots \text{(a)}$$

Also:

$$\Delta H_f P_1 = \Delta H_f (P_1 - H)^- + \Delta H_f H^+ - PA(P_1 - H)^-$$

$$\Delta H_f P_2 = \Delta H_f (P_2 - H)^- + \Delta H_f H^+ - PA(P_2 - H)^-$$

Subtract:

$$\Delta H_f P_1 - \Delta H_f P_2 = - (PA(P_1 - H)^- - PA(P_2 - H)^-) + \Delta H_f (P_1 - H)^- - \Delta H_f (P_2 - H)^- \quad \text{(b)}$$

Put (b) in (a):

$$\Delta = Ca_{aff}(P_1 - H)^- - Ca_{aff}(P_2 - H)^- - (PA(P_1) - PA(P_2)) - (PA(P_1 - H)^- - PA(P_2 - H)^-) + \Delta H_f [P_2 - H]^- - \Delta H_f [P_1 - H]^- - \Delta H_f (P_1 - H)^- + \Delta H_f (P_2 - H)^-$$

$$\Delta = \Delta C_{aff} [P-H]^- - \Delta PA(P) - \Delta PA (P-H)^- \quad (1)$$

3. $(P_1-2H)^{2-} \cdots Ca^{2+} \cdots (P_2-2H)^{2-}$ dissociating to $[(P_1-3H)^{3-} + Ca^{2+}] + (P_2-H)^-$ or to $[(P_2-3H)^{3-} + Ca^{2+}] + (P_1-H)^-$

$$\Delta H_f [(P_1-H)^- \cdots Ca^{2+} \cdots (P_2-3H)^{3-}] \rightarrow \Delta H_f (P_1-2H)^{2-} + \Delta H_f H^+ - PA(P_1-2H)^{2-} + \Delta H_f (P_2-3H)^{3-} + \Delta H_f Ca^{2+} - C_{aff} (P_2-3H)^{3-}$$

$$\Delta H_f [(P_2-H)^- \cdots Ca^{2+} \cdots (P_1-3H)^{3-}] \rightarrow \Delta H_f (P_2-2H)^{2-} + \Delta H_f H^+ - PA(P_2-2H)^{2-} + \Delta H_f (P_1-3H)^{3-} + \Delta H_f Ca^{2+} - C_{aff} (P_1-3H)^{3-}$$

Subtract

$$\Delta = \Delta H_f (P_1-2H)^{2-} - \Delta H_f (P_2-2H)^{2-} - PA(P_1-2H)^{2-} + PA (P_2-2H)^{2-} + \Delta H_f (P_2-3H)^{3-} - \Delta H_f (P_1-3H)^{3-} - C_{aff} [P_2-3H]^{3-} + C_{aff} [P_1-3H]$$

$$\Delta = C_{aff} [P_1-3H]^{3-} - C_{aff} [P_2-3H]^{3-} + \Delta H_f (P_1-2H)^{2-} - \Delta H_f (P_2-2H)^{2-} + \Delta H_f (P_2-3H)^{3-} - \Delta H_f (P_1-3H)^{3-} \quad (c)$$

Also:

$$\Delta H_f (P_1-2H)^{2-} = \Delta H_f (P_1-3H)^{3-} + \Delta H_f H^+ - PA [P_1-3H]^{3-}$$

$$\Delta H_f (P_2-2H)^{2-} = \Delta H_f (P_2-3H)^{3-} + \Delta H_f H^+ - PA (P_2-3H)^{3-}$$

Subtract:

$$\Delta H_f (P_1-2H)^{2-} - \Delta H_f (P_2-2H)^{2-} = \Delta H_f (P_1-3H)^{3-} - \Delta H_f (P_2-3H)^{3-} - PA [P_1-3H]^{3-} + PA [P_2-3H]^{3-} \quad (d)$$

Put (d) in (c):

$$\Delta = C_{aff} [P_1-3H]^{3-} - C_{aff} [P_2-3H]^{3-} - (PA(P_1-2H)^{2-} - PA (P_2-2H)^{2-} + \Delta H_f (P_1-3H)^{3-} - \Delta H_f (P_2-3H)^{3-} - PA [P_1-3H]^{3-} + PA [P_2-3H]^{3-} + \Delta H_f (P_2-3H)^{3-} - \Delta H_f (P_1-3H)^{3-})$$

$$\Delta = C_{aff} [P_1-3H]^{3-} - C_{aff} [P_2-3H]^{3-} - (PA(P_1-2H)^{2-} - PA (P_2-2H)^{2-}) - (PA(P_1-3H)^{3-} - PA (P_2-3H)^{3-})$$

$$\Delta = \Delta C_{aff} (P-3H)^{3-} - \Delta PA (P-2H)^{2-} - \Delta PA (P-3H)^{3-} \quad (2)$$