CHAPTER IV

CONCLUSION

The capacity of exchanged cations of Bang Rin kaolinite, bentonite and marl with various cations in both single exchangeable cations and mixed exchangeable cations methods were determined by atomic absorption spectrophotometry and flame photometry. The CEC in both methods apparently decreased in the order:

Bentonite > Kaolinite > Marl

The orders of CEC in these materials in the single exchangeable cations method are all different. In kaolinite the CEC seemed to increase as the size of the exchanging ion decreased. In general the values of individual mixed CEC's are higher than those of the corresponding CEC.

The formation of intercalation complexes of kaolinite, bentonite and marl was studied using X-ray diffraction and IR spectroscopic techniques. From the x-ray diffraction patterns it was found that all organic reagents were capable of forming intercalation complexes with kaolinite, but could not complex with marl or bentonite.

In the study of intercalation of inorganic salts into kaolinite, bentonite and marl it was found that only CH_3COOK could penetrate into the interlayer space of kaolinite, thus forming an intercalation compound. For marl and bentonite none of the salts were capable of forming an intercalation complex. From IR study, only dimethylsulfoxide (DMSO) could form an intercalation complex with kaolinite. None of organic compounds could complex with bentonite and marl.

In this study, the CEC's of marl for Fe^{2+} and Fe^{3+} are zero whilst Ca^{2+}, Na^{+}, K^{+} and Zn^{2+} were found to be adsorbed by marl. If marl were used for the prevention of iron overload, the levels of these other ions in food may also be affected.

Since bentonite has a higher CEC than kaolinite and marl in both single and mixed ion methods, and it was found that bentonite cannot form an intercalation complex with paraquat, it is suggested that paraquat was adsorbed only on the surface of bentonite. Also, in view of the fact that an intercalated complex can be formed between kaolinite and paraquat, it may be possible that kaolinite can act as an immediate antidote to paraquat poisoning.

The interlayer hydrogen bond lengths and strength in kaolinite were calculated using Lennard-Jone potential function and semiempirical potential function, respectively. The calculated bond energies were within limits for hydrogen bonds which can be described in term of a linear model.

APPENDIX

APPENDIX I

CHARACTERISATION OF KAOLINITE SAMPLE FROM

BANG RIN, RANONG, THAILAND

Table A.1 Geological Data (43)

1.	Type of deposits	hydrothermal
2.	Size of deposits	intermediate
3.	Proven depth of kaolinization (m)	1.0
4.	Thickness of overburden (m)	-
5.	Parent rocks	granite
6.	Age of parent rocks	Mesozoic
7.	Genetic type	residual
8.	Morphological type	irregular

Table A.2 Index Properties (43)

1.	Thermal expansion	$(30\text{-}40^{\circ}C)\ 10^{-6}$	5.3
2.	Water absorption	(% at $1200^{\circ}C$)	32.7
3.	Total shrinkage	(%at $1200^{\circ}C$)	7.8
4.	Modulus of rupture	(lb/in^2)	10.2
5.	Refractoriness	($^{\circ}C$)	1785
6.	Fired color	(at $1200^{\circ}C$)	white

Table A.3 Chemical analysis and clay mineral content (43)

1. Chemical composition :

SiO_2	46.88
Al_2O_3	39.56
K_2O	0.49
Na_2O	0.39
MgO	0.35
CaO	0.25
Fe_2O_3	0.24
MnO	0.21
TiO_2	nil

2. Major clay minerals   kaolinite

APPENDIX II

THE CALIBRATION CURVES FOR INORGANIC IONS

The calibration curves were obtained by measuring the absorbance at 213.9, 248.3, 422.7 and 589.0 nm for Zn, Fe, Ca, and Na respectevely using an Instrumentation Laboratory Atomic Absorption Spectrophotometer model 457. Only the calibration curve for Ca was obtained by employing a Corning 400 flame photometer. Results are shown in Figure A.1-A.5.
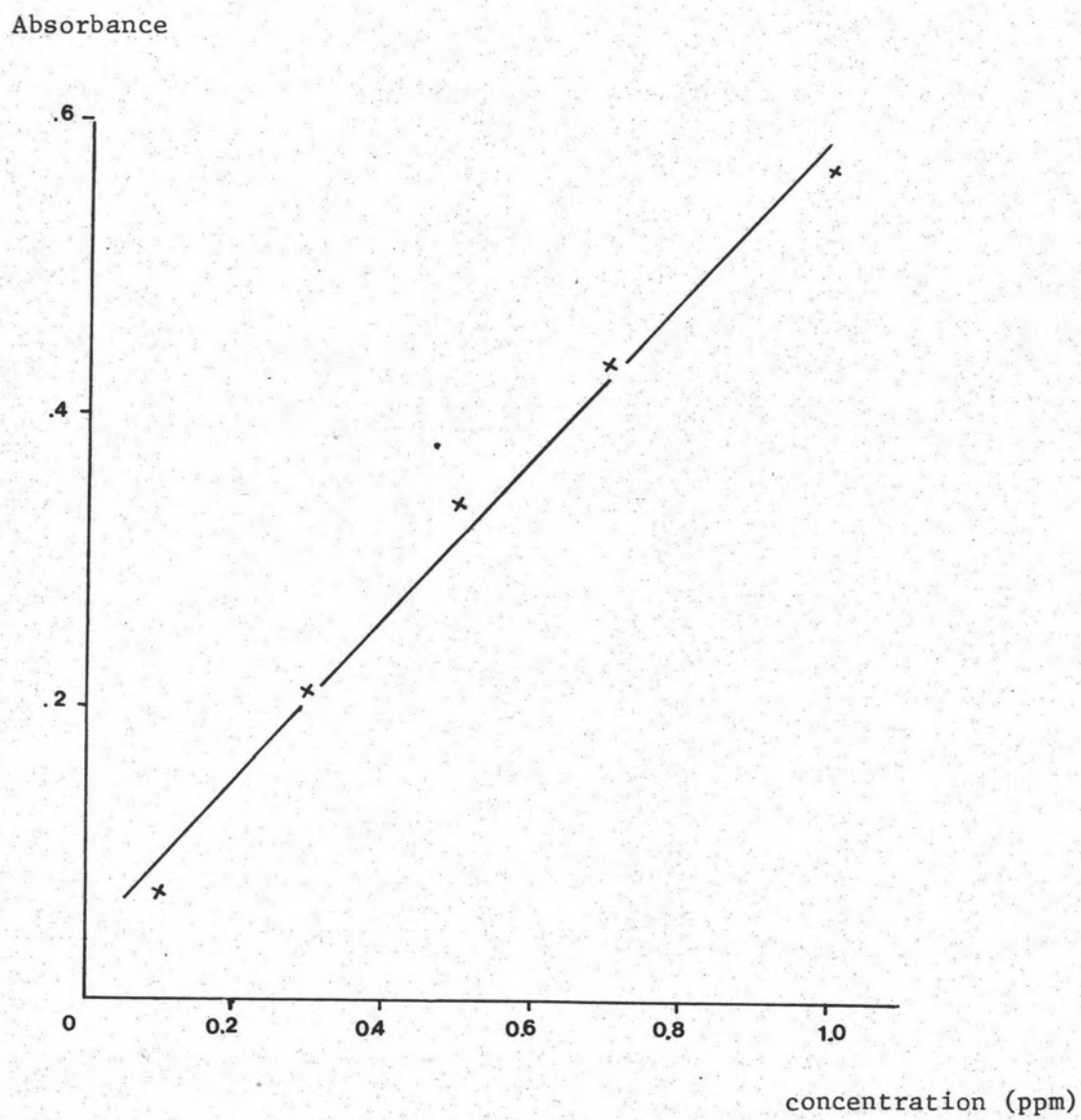
Absorbance

Figure A.1 Plot of absorbance VS. zinc ion concentration
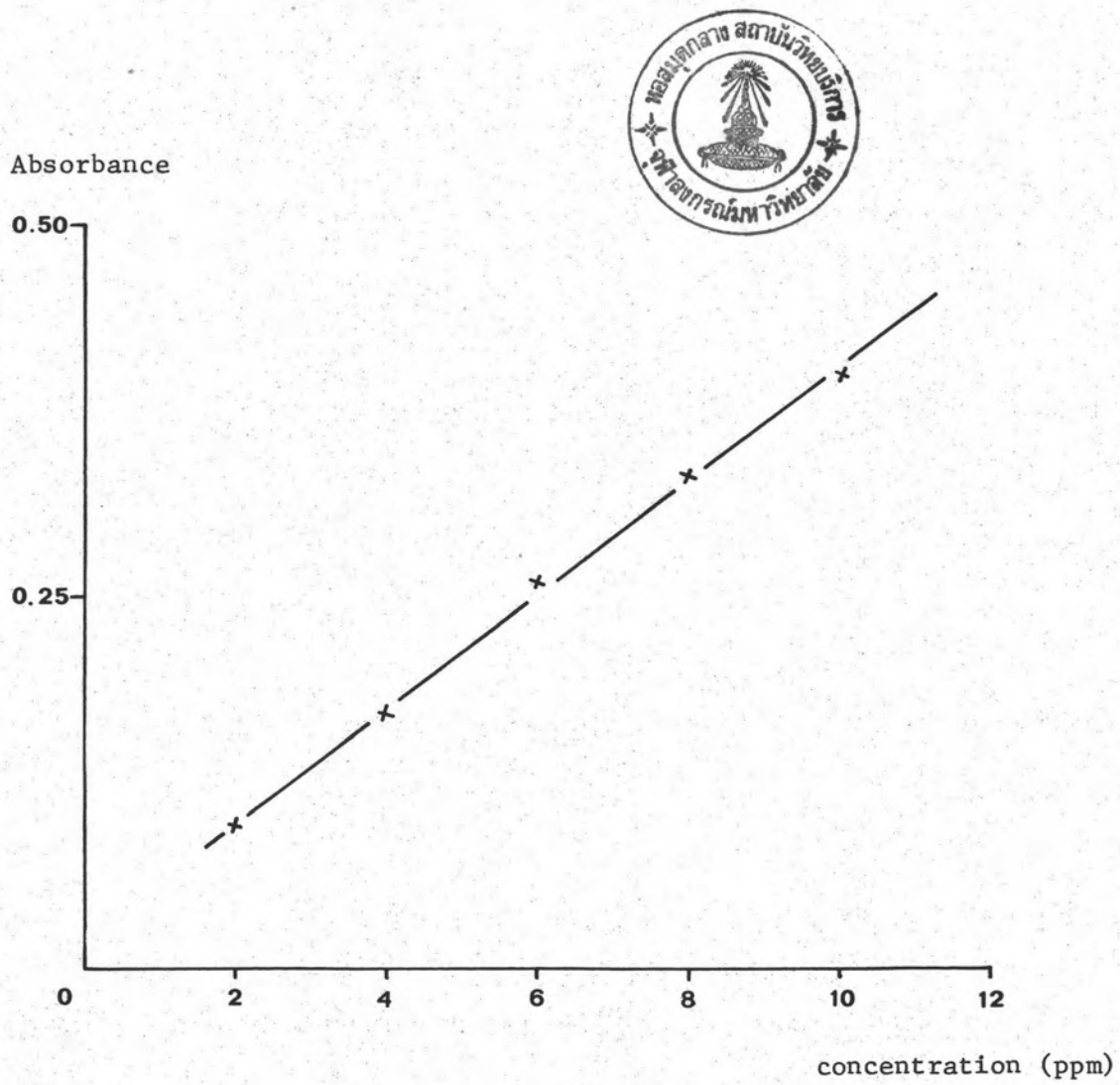
Absorbance

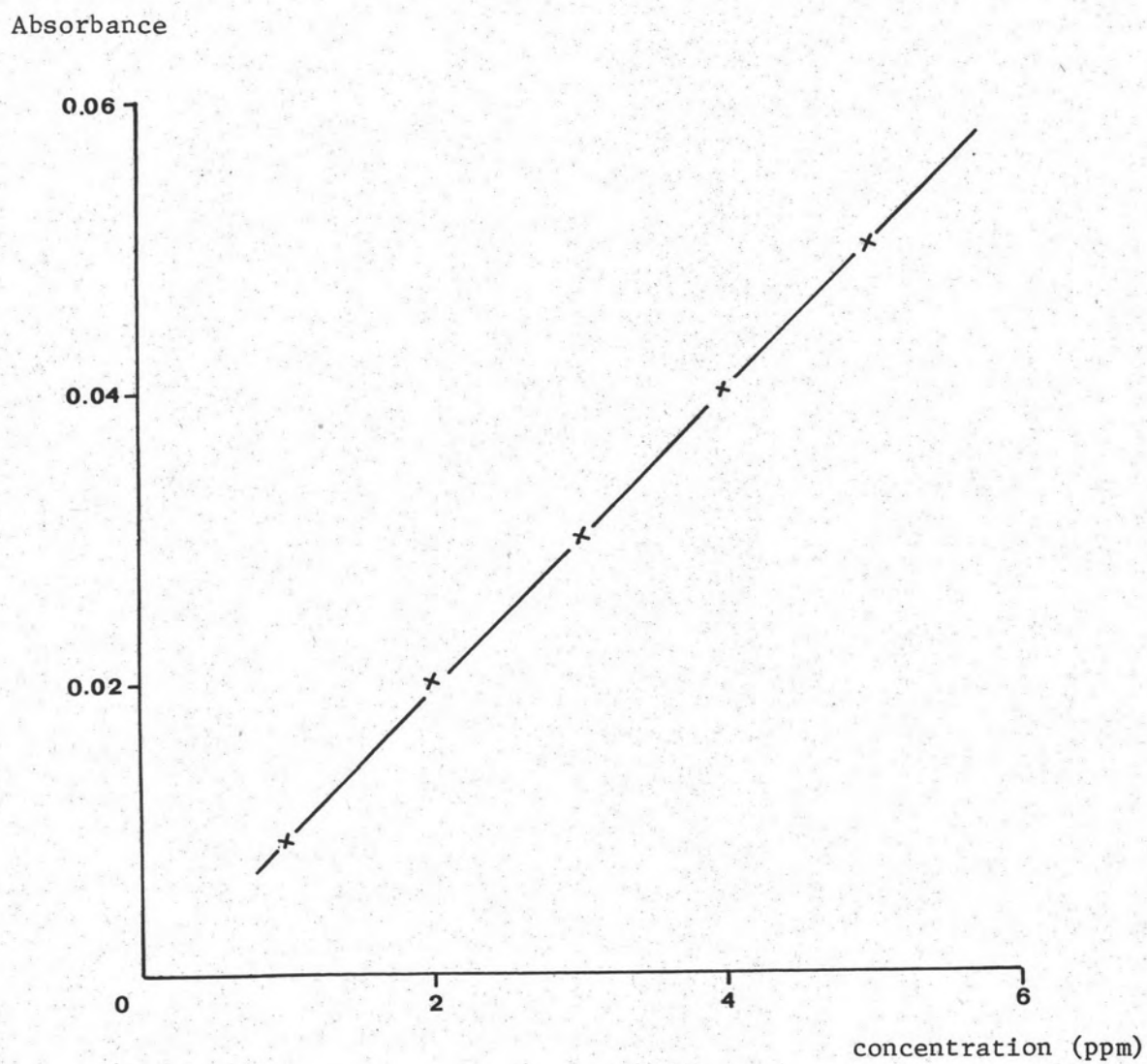Figure A.2 Plot of absorbance VS. Iron concentration

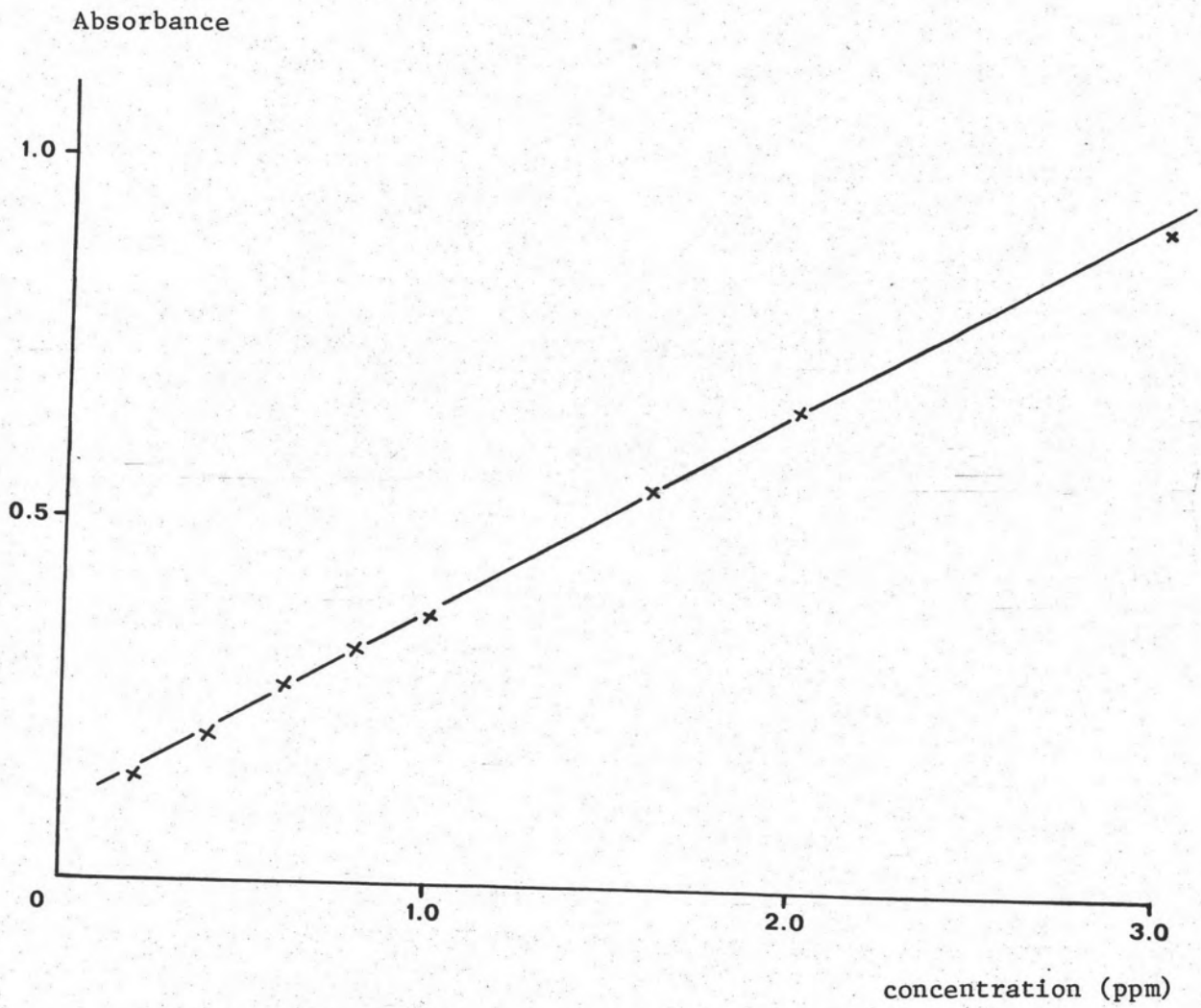Figure A.3 Plot of absorbance VS. calcium ion concentration

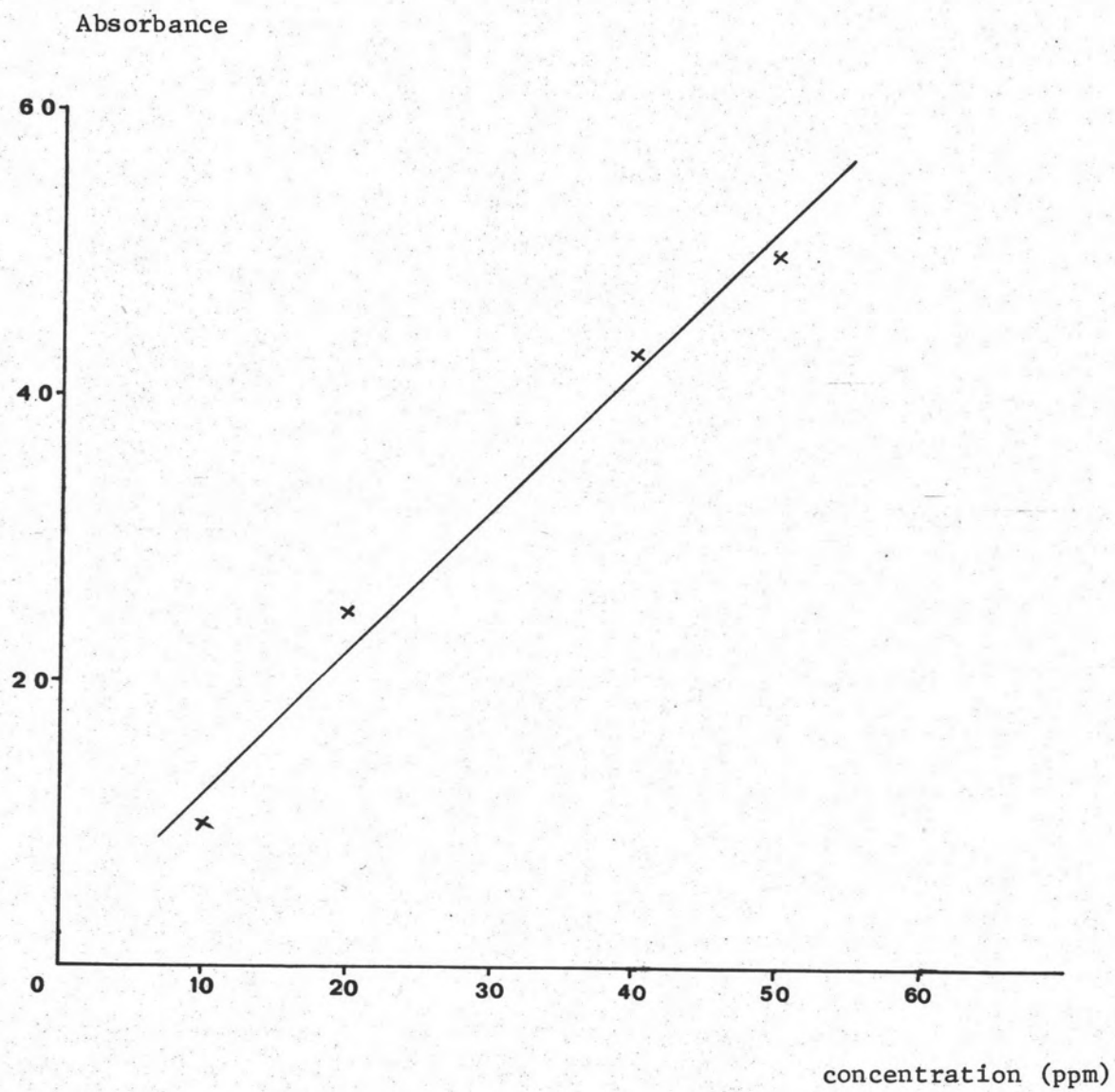Figure A.4 Plot of absorbance VS. sodium ion cencentration

Figure A.5 Plot of absorbance VS. potassium ion concentration

Appendix III

Hydrogen Bond Length Calculation

$$\Delta = 50 \left[\left(\frac{d}{R}\right)^{12} - \left(\frac{d}{R}\right)^{6} \right]$$

1. For $\Delta = 90$, $(3742-3652)$ cm^{-1}

    $d = 2.8$ Å, the sum of the Van der Waals radii of oxygen atoms in

    the OH---O bond

substitution of these values in the above equation gives

$$90 = 50 \left[\frac{232218.27}{R^{12}} - \frac{481.89}{R^{6}} \right]$$

$$1.8 = \frac{232218.27 - 481.89 \, R^{6}}{R^{12}}$$

$$1.8 \, R^{12} + 481.89 \, R^{6} - 232218.27 = 0$$

$$R^{6} = \frac{-b \pm \sqrt{b^{2} + 4ac}}{2a}$$

$$= \frac{-481.89 \pm \sqrt{(481.89)^{2} + 4 \times 1.8 \times 232218.27}}{2 \times 1.8}$$

$$= \frac{-481.89 \pm 1379.92}{3.60}$$

$$\therefore R = 2.51$$

2. For $\Delta = 75$, $(3742-3667)$ cm^{-1}

$$75 = 50 \left[\left(\frac{2.8}{R}\right)^{12} - \left(\frac{2.8}{R}\right)^{6} \right]$$

$$1.5 = \frac{232218.27 - 481.89 \ R^{6}}{R^{12}}$$

$$1.5 \ R^{12} + 481.89 \ R^{6} - 232218.27 = 0$$

$$R^{6} = \frac{-b \pm \sqrt{b^{2} + 4ac}}{2a}$$

$$= \frac{-481.89 \pm \sqrt{232218.27 + 1393309.6}}{2 \times 1.5}$$

$$= \frac{-481.89 \pm 1274.96}{3}$$

$$R^{6} = 585.62$$

$$\therefore R = 2.53$$

3. For $\Delta = 51$, $(3742-3691)$ cm^{-1}

$$51 = 50 \left[\left(\frac{2.8}{R}\right)^{12} - \left(\frac{2.8}{R}\right)^{6} \right]$$

$$1.02 = \frac{232218.27 - 481.89 \ R^{6}}{R^{12}}$$

$$1.02 \ R^{12} + 481.89 \ R^{6} - 232218.27 = 0$$

$$R^{6} = \frac{-b \pm \sqrt{b^{2} + 4ac}}{2a}$$

$$= \frac{-481.89 \pm \sqrt{232218.27 + 947450.52}}{2.04}$$

$$= \frac{-481.89 \pm 1086.13}{2.04}$$

$$\therefore R = 2.58$$

Appendix IV

Hydrogen Bond Energy Calculation

1. For $R = 2.51$ Å, $r = 1.11$ Å, $r^* = 1.40$ Å.

$$
\begin{aligned}
1.1 \quad V_1 &= D_o \left[1 - \exp(-\alpha) \right] \\
&= 493.71 \text{ kJ/mol} \left[1 - \exp(-0.08) \right] \\
&= 493.71 \text{ kJ/mol} \left(1 - 0.92 \right) \\
&= 493.71 \text{ kJ/mol} \ (0.08) \\
&= 39.50
\end{aligned}
$$

$$
\begin{aligned}
1.2 \quad V_2 &= D_o^* \left[1 - \exp(-\beta) \right] - D_o^* \\
&= 0.56 \times 10^{-18} \text{ Nm} \left[1 - \exp(0.88) \right] - 0.56 \times 10^{-18} \text{ Nm} \\
&= 0.56 \times 10^{-18} \text{ Nm} \times 0.59 - 0.56 \times 10^{-18} \text{ Nm} \\
&= 0.33 \times 10^{-18} \text{ Nm} - 0.56 \times 10^{-18} \text{ Nm} \\
&= -0.23 \times 10^{-18} \text{ Nm} \\
&= -138 \text{ kJ/mol}
\end{aligned}
$$

$$
\begin{aligned}
1.3 \quad V_3 + V_4 &= A \left[e^{-bR} - (\tfrac{1}{2})(R_o/R)^m e^{-bR_o} \right] \\
&= 18.06 \times 10^6 \text{ kJ/mol} \left[5.84 \times 10^{-6} - \tfrac{1}{2} \times 5.84 \times 10^{-6} \right] \\
&= 18.06 \times 10^6 \text{ kJ/mol} \left[5.84 \times 10^{-6} - 2.92 \times 10^{-6} \right] \\
&= 18.06 \times 10^6 \text{ kJ/mol} \left(2.96 \times 10^{-6} \right) \\
&= 52.73 \text{ kJ/mol}
\end{aligned}
$$

$$
\begin{aligned}
1.4 \quad V &= V_1 + V_2 + V_3 + V_4 \\
&= 39.50 + (-1.38) + 52.73 \text{ kJ/mol} \\
&= -45.76 \text{ kJ/mol}
\end{aligned}
$$

2. For $R = 2.53$ Å, $r = 1.09$ Å, $r^* = 1.44$ Å

   2.1 V_1 = $D_o \left[1 - \exp(-\alpha) \right]$

          = 493.71 kJ/mol $\left[1 - \exp(-0.06) \right]$

          = 493.71 kJ/mol $\left(1 - 0.94 \right)$

          = 493.71 kJ/mol (0.06)

          = 29.62 kJ/mol

   2.2 V_2 = $D_o^* \left[1 - \exp(-\beta) \right] - D_o^*$

          = 0.56×10^{-18} Nm $\left[1 - \exp(-1.02) \right] - 0.56 \times 10^{-18}$ Nm

          = 0.56×10^{-18} Nm $\left[1 - (0.36) \right] - 0.56 \times 10^{-18}$ Nm

          = 0.56×10^{-18} Nm $(0.64) - 0.56 \times 10^{-18}$ Nm

          = 0.36×10^{-18} Nm $- 0.56 \times 10^{-18}$ Nm

          = 0.20×10^{-18} Nm

          = -120 kJ/mol

   2.3 $V_3 + V_4$ = $A \left[e^{-bR} - (\tfrac{1}{2})(R_o/R)^m \, e^{-bR_o} \right]$

          = 18.06×10^6 kJ/mol $\left[5.32 \times 10^{-6} - (\tfrac{1}{2})(5.32 \times 10^{-6}) \right]$

          = 18.06×10^6 kJ/mol $\left[5.32 \times 10^{-6} - 2.66 \times 10^{-6} \right]$

          = 18.06×10^6 kJ/mol (2.66×10^{-6})

          = 48.04 kJ/mol

   2.4 V = $V_1 + V_2 + V_3 + V_4$

          = $29.62 + (-120) + 48.04$ kJ/mol

          = -42.34 kJ/mol

3. For $R = 2.53$ Å, $r = 1.06$ Å, $r^* = 1.52$ Å

   3.1 V_1 = $D_o \left[1 - \exp(-\alpha) \right]$

          = 493.71 kJ/mol $\left[1 - \exp(-0.035) \right]$

          = 493.71 kJ/mol $\left(1 - 0.965 \right)$

          = 17.28 kJ/mol

$$3.2 \quad V_2 = D_o^* \left[1-\exp(-\beta)\right] - D_o^*$$

$$= 0.56 \times 10^{-18} \text{ Nm} \left[1-\exp(-1.32)\right] - 0.56 \times 10^{-18} \text{ Nm}$$

$$= 0.56 \times 10^{-18} \text{ Nm} \left(1-0.27\right) - 0.56 \times 10^{-18} \text{ Nm}$$

$$= 0.56 \times 10^{-18} \text{ Nm} (0.73) - 0.56 \times 10^{-18} \text{ Nm}$$

$$= -0.15 \times 10^{-18} \text{ Nm}$$

$$= -90 \text{ kJ/mol}$$

$$3.3 \quad V_3 + V_4 = A \left[e^{-bR} - (\tfrac{1}{2})(R_o/R)^m e^{-bR_o}\right]$$

$$= 18.06 \times 10^6 \text{ kJ/mol} \left[4.185 \times 10^{-6} - 2.09 \times 10^{-6}\right]$$

$$= 18.06 \times 10^6 \text{ kJ/mol} (2.09 \times 10^{-6})$$

$$= 37.79 \text{ kJ/mol}$$

$$3.4 \quad V = V_1 + V_2 + V_3 + V_4$$

$$= 17.28 + (-90) + 37.79 \text{ kJ/mol}$$

$$= -34.93 \text{ kJ/mol}$$