CHAPTER V

DISCUSSIONS

5.1 Improved Capillary Method

In this experiment, the diffusion cell was so developed and constructed that disturbance and natural convection effects were minimized. The diffusion cell was a capillary type and its details were presented in chapter 3.

Dye studied with potassium permanganate showed that when a capillary tube was used without collar (tube holder), there was a stream of potassium permanganate moving downward. This indicated that natural convection took place, as shown in Fig 5.1. But when a capillary tube was used with collar at its mouth, the convection effect was eliminated as shown in Fig 5.2

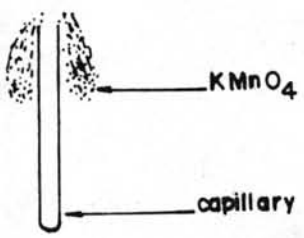

Figure 5.1 Illustration of $KMnO_4$ experiment showing evidence of natural convection.

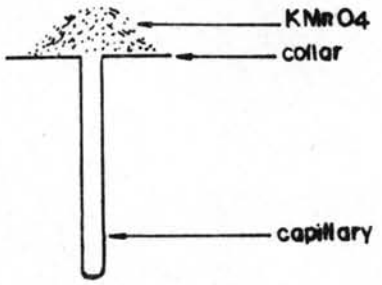

Figure 5.2 Illustration of $KMnO_4$ experiment showing arrangement of capillary for minimization of natural convection.

Disturbance was minimized by using a pneumatic system for removing the capillary cap. It was observed in an experiment with $KMnO_4$ solution that the dye did not come out off the capillary mouth at the time of capillary cap removal. This observation demonstrated that the error associated with starting the experiment was not considerable.

The improved capillary cell offerred a simple, rapid and inexpensive equipment. It costs less than 400 Baht. It can be extended to measurements under extreme conditions which rendered other techniques unsuitable. It requires little amount of solution and very little amount of solute.

5.2 Calculation of Diffusivities

Equation (2.30) to Eq. (2.39) were used in solving for diffusivities. One - dimensional diffusion was used in the capillary,

and full three - dimensional diffusion was used from the capillary mouth. A computer program was written as presented in Table 5.1 to back calculate diffusivities. The correct diffusivity value was determined with the aid of the Fibonacci Search. Its simplified flow chart was shown in Fig. 5.3

Table 5.1 Computer Program of Diffusivity

```
C       CALCULATION OF DIFFUSION COEFFICIENT
        DIMENSION C(12), CNEW(12), C3(11,11,11), C3NEW(11,11,11)
        DO 11 M = 1,28
        READ (5,901) CPL,EXPTT,BIGCI,BIGCF,VOL
        READ (5,902) DL,DU
  555   READ (5,900,END=1000) IMAX,JMAX,DIVX,DIVT
        WRITE (6,900) IMAX, JMAX, DIVX, DIVT
        WRITE (6,901) CPL,EXPTT,BIGCI,BIGCF,VOL
        WRITE (6,902) DL,DU
        IMAX1 = IMAX+1
        IMAX2 = IMAX+2
        JMAX1 = JMAX+1
        II = IMAX-1
        DELX = 1./DIVX
        EPS = 0.0000001
        SUMC = BIGCF*VOL
        WRITE (6,904) SUMC
C       FIBONACCI SEARCH
   20   DLL = (3./8.)*(DU-DL)+DL
        D = DLL
        GONUM = -1.
        GO TO 30
   21   DUU = (5./8.)*(DU-DL)+DL
        D  = DUU
        GONUM = 1.
        GO TO 30
   22   CONTINUE
        IF (DUU-DLL-EPS) 23,23,24
   23   D   = (DUU+DLL)/2.
        GO TO 100
   24   IF (FUNCU-FUNCL) 25,25,26
   25   DL  = DLL
        GO TO 20
   26   DU  = DUU
        GO TO 20
   30   THAL = D*EXPTT/CPL**2
        DELT = THAL/DIVT
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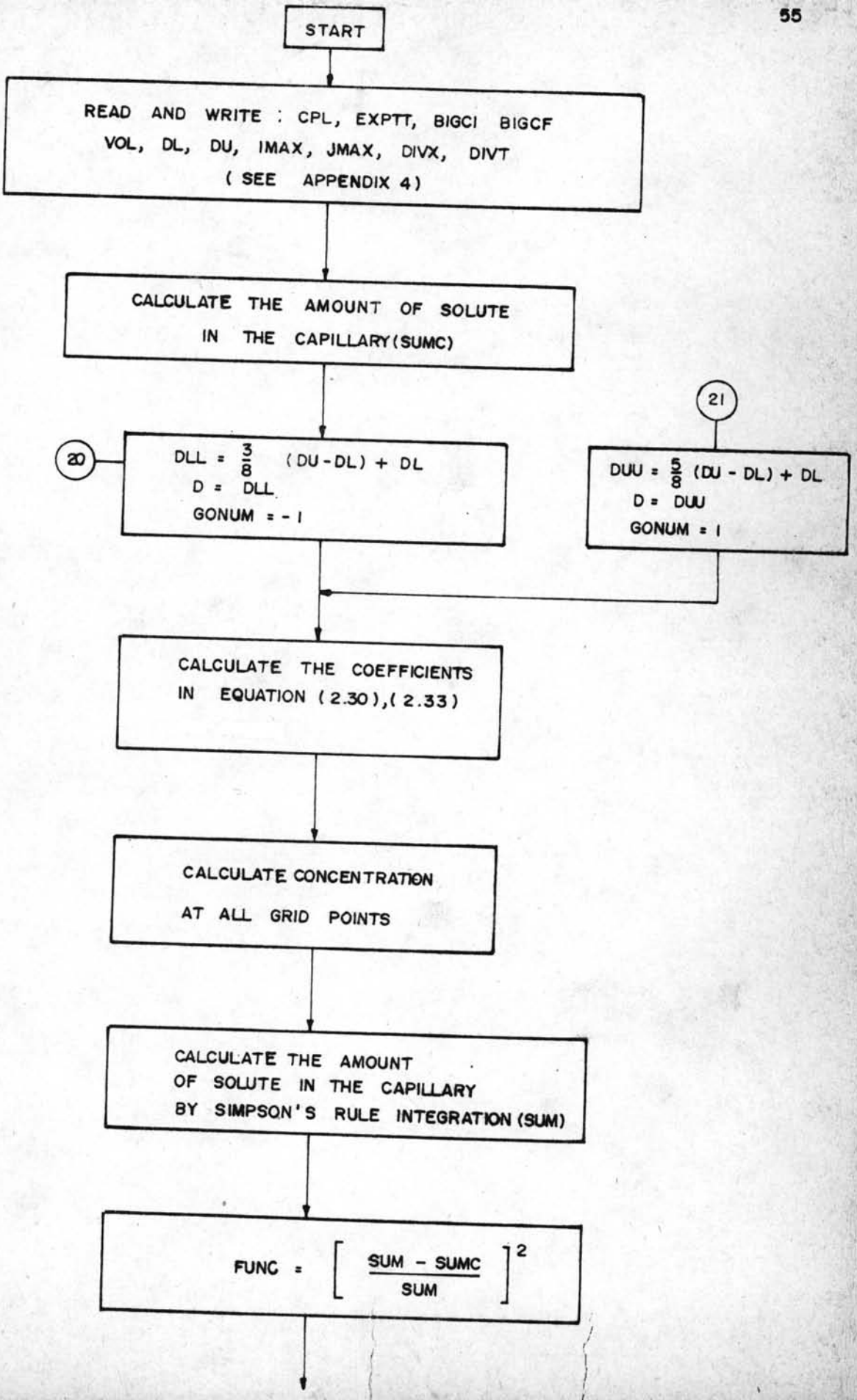
```
      COEF2 = DELT/DELX**2
      COEF1 = 1.-2.*COEF2
      COEF3 = COEF2
      COEF4 = COEF2
      COEF = 1.-2.*COEF2-2.*COEF3-2.*COEF4
      DO 200 I =1,IMAX1
  200 C(I) = 1.0
      DO 40 I=1,IMAX1
      DO 40 L=1,IMAX1
      DO 40 K=1,IMAX1
      C3NEW(I,L,K)=0.0
   40 C3(I,L,K) = 0.0
      DO 106 J = 1,JMAX
      CNEW (1) = COEF1*C(1)+2.*COEF2*C(2)
      DO 101 I = 2,IMAX
      CNEW (I) = COEF1*C(I)+COEF2*(C(I+1)+C(I-1))
  101 CONTINUE
      CNEW(IMAX1)=(C(IMAX)+C3(2,1,1)+C3(1,2,1)+C3(1,1,2))/4.
      C3NEW(1,1,1)=CNEW(IMAX1)
      DO 41 I=2,IMAX
   41 C3NEW(I,1,1)  = COEF*C3(I,1,1)+COEF2*(C3(I-1,1,1)+C3(I+1,1,1))
     C+COEF3*2.*C3(I,2,1)+COEF4*2.*C3(I,1,2)
      DO 50 L=2,IMAX
   50 C3NEW(1,L,1)  = COEF*C3(1,L,1)+2.*C3(2,L,1)*COEF2
     C+COEF3*(C3(1,L-1,1)+C3(1,L+1,1))+2.*COEF4*C3(1,L,2)
      DO 51 K=2,IMAX
   51 C3NEW(1,1,K)  = COEF*C3(1,1,K)+2.*C3(2,1,K)*COEF2
     C+2.*COEF3*C3(1,2,K)+COEF4*(C3(1,1,K-1)+C3(1,1,K+1))
      DO 60 I=2,IMAX
      DO 60 K=2,IMAX
      C3NEW(I,1,K)=COEF*C3(I,1,K)+COEF2*(C3(I-1,1,K)
     C+C3(I+1,1,K))+2.*COEF3*C3(I,2,K)
     C+COEF4*(C3(I,1,K-1)+C3(I,1,K+1))
   60 CONTINUE
      DO 61 I=2,IMAX
      DO 61 L=2,IMAX
      C3NEW(I,L,1)=COEF*C3(I,L,1)+COEF2*(C3(I-1,L,1)
     C+C3(I+1,L,1))+COEF3*(C3(I,L-1,1)+C3(I,L+1,1))
     C+2.*COEF4*C3(I,L,2)
   61 CONTINUE
      DO 42 K=2,IMAX
      DO 42 L=2,IMAX
      C3NEW(1,L,K)  = COEF*C3(1,L,K)+2.*COEF2*C3(2,L,K)
     C+COEF3*(C3(1,L-1,K)+C3(1,L+1,K))
     C+COEF4*(C3(1,L,K-1)+C3(1,L,K+1))
      DO 43 I=2,IMAX
   43 C3NEW(I,L,K) = COEF*C3(I,L,K)+COEF2*(C3(I-1,L,K)+C3(I+1,L,K))
     C+COEF3*(C3(I,L-1,K)+C3(I,L+1,K))
     C+COEF4*(C3(I,L,K-1)+C3(I,L,K+1))
   42 CONTINUE
```

```
      DO 105 I = 1,IMAX1
      C(I) = CNEW(I)
  105 CONTINUE
      DO 45 I=1,IMAX
      DO 45 L=1,IMAX
      DO 45 K=1,IMAX
   45 C3(I,L,K) = C3NEW(I,L,K)
  106 CONTINUE
C     CALCULATION OF TOTAL QUANTITY BY SIMPSON RULE
      SUM = 0.
      DO 300 I = 1,II,2
  300 SUM = SUM+(DELX/3.)*(C(I)+4.*C(I+1)+C(I+2))
      SUM = BIGCI*SUM*VOL
      FUNC = ((SUM-SUMC)/SUM)**2
      WRITE (6,905) (C(I),I=1,IMAXI)
      WRITE (6,906) D,SUM,FUNC
      IF(GONUM) 35,35,36
   35 FUNCL = FUNC
      GO TO 21
   36 FUNCU = FUNC
      GO TO 22
  100 CONTINUE
      WRITE (6,907) D
   11 CONTINUE
 1000 STOP
  900 FORMAT (2I5,2F10.2)
  901 FORMAT (5F13.5)
  902 FORMAT (2F15.7)
  904 FORMAT (//6X,28HTOTAL AMOUNT BY EXPERIMENT =,F15.7)
  905 FORMAT ((6E15.7)/)
  906 FORMAT (/8X,3HD =,E15.5,8X,9HCAVE/CI =,E15.5,8X,
     C10HERROR-SQ =,E15.5)
  907 FORMAT (//10X,14HCALCULATED D =,E15.5)
      END
```


START
READ AND WRITE : CPL, EXPTT, BIGCI BIGCF
VOL, DL, DU, IMAX, JMAX, DIVX, DIVT
(SEE APPENDIX 4)
CALCULATE THE AMOUNT OF SOLUTE
IN THE CAPILLARY(SUMC)
20
DLL = 3/8 (DU-DL) + DL
D = DLL
GONUM = -1
21
DUU = 5/8 (DU - DL) + DL
D = DUU
GONUM = 1
CALCULATE THE COEFFICIENTS
IN EQUATION (2.30),(2.33)
CALCULATE CONCENTRATION
AT ALL GRID POINTS
CALCULATE THE AMOUNT
OF SOLUTE IN THE CAPILLARY
BY SIMPSON'S RULE INTEGRATION (SUM)
FUNC = [SUM - SUMC / SUM]^2

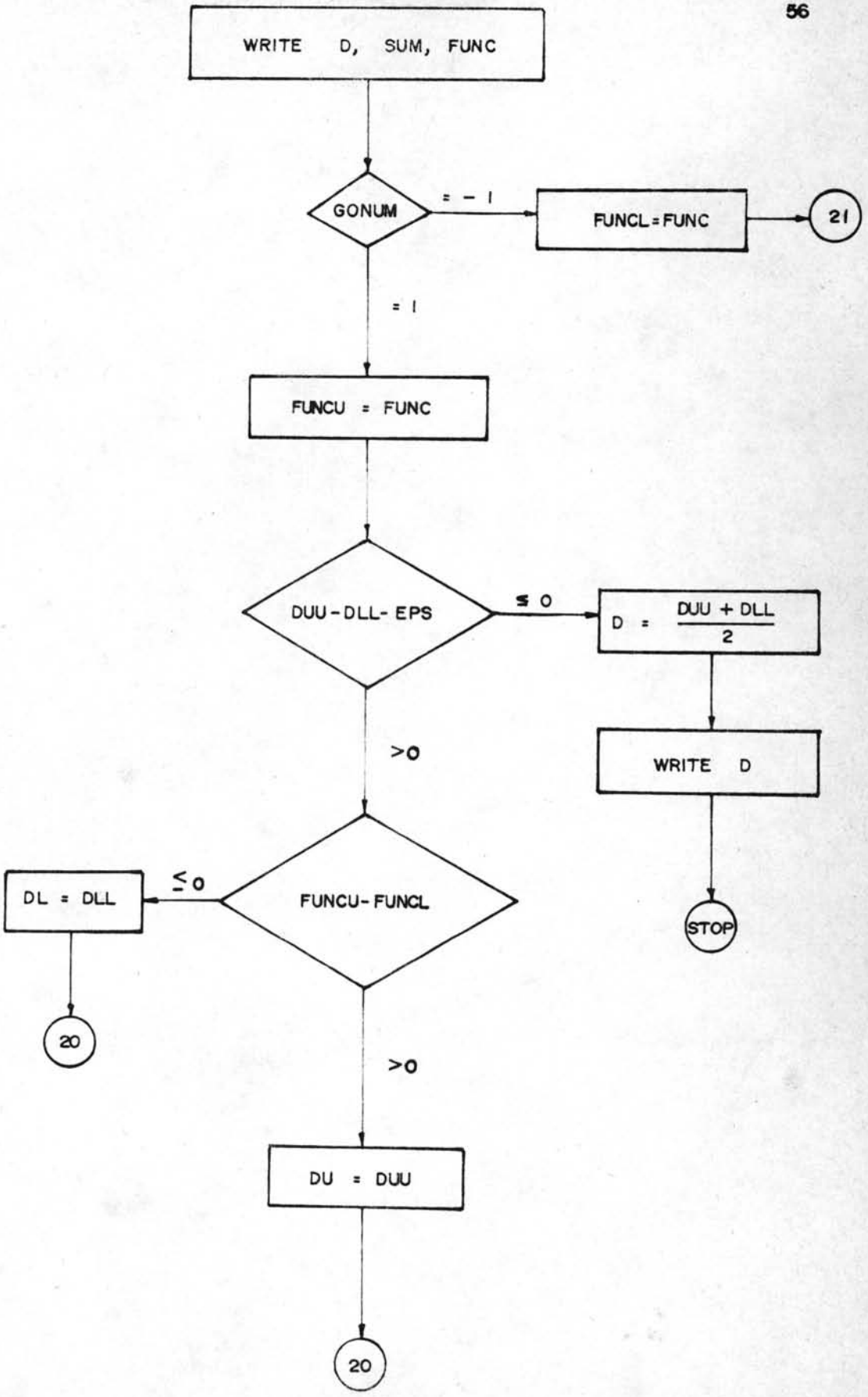


Figure. 5.3 Flow chart of diffusivity.

The stability of the finite difference calculations required that λ_1, λ_2 and λ_3 be smaller than 0.5. Ten grid points, which was recommended by Nanis[23], in the capillary ($\Delta\eta = 0.1$) was used. The same step size ($\Delta\eta = \Delta\beta = \Delta\xi = 0.1$) was used in the three - dimensional diffusion region. The dimensionless concentrations at all grid points were carried out. And also, the dimensionless concentrations in the three - dimensional diffusion region were calculated step by step from the mouth of the capillary to the infinite medium (concentration = 0)

A 20 time increments was used in all calculations. This value was tested with KCl data to give satisfactory accuracy. With numbers of time increments of 20. 30, 40 and 50, the values of diffusivity obtained were 1.98×10^{-5}, 1.94×10^{-5}, 1.92×10^{-5} and 1.91×10^{-5} $cm^2/sec.$ respectively.

5.3 Calibration of the Capillary Cell

In this experiment, KCl solution was used to calibrate the equipment. The diffusivity of 1 N KCl at 27.8°C was shown in Table 4.1. Its average value was 2.18×10^{-5} $cm^2/sec.$ and was good comparing with Fell's value[24] of 2.07×10^{-5} $cm^2/sec.$ The overall difference was about 6 % due to weighting, measuring and computation errors.

5.4 Analysis of $Th(NO_3)_4$ Solutions.

$Th(NO_3)_4$ solutions contained not only thorium but also its many daughter substances (see Appendix 3). However, the amount of daughter substances compared to that of thorium were so small that they might be negligible. Analysis of thorium was done through detection of one of its daughters, tallium 208, by gamma - ray spectrometer. The $Th(NO_3)_4$ solutions were analysed a day after diffusion experiment to make sure that

the original tallium at the time of diffusion had already decayed.

5.5 Effect of Temperature on Diffusivities

The diffusivities of $Th(NO_3)_4$ increased with increasing in temperature. A plot of log D versus $\frac{1}{T}$ gave a straight line of negative slope, as shown in Fig. 4.1. These lines were drawn by the method of least squares. These lines could be expressed in the following equation: $D = D_o e^{-E/T}$, where E is a constant. Experiments showed that E depended on the concentration as in Fig. 4.3.

5.6 Effect of Concentration on Diffusivities

The diffusivity of $Th(NO_3)_4$ in nitric acid solution decreased nonlinearly as the concentration increased as shown in Table 4.2 and Fig. 4.2. The curves in Fig 4.2 were drawn according to the following equations.

$D = 10^{-5} (1.539 - 3.852\ c + 2.504\ c^2)$ for 0.05 M solution

$D = 10^{-5} (2.201 - 4.556\ c + 2.559\ c^2)$ for 0.1 M solution

$D = 10^{-5} (2.208 - 4.305\ c + 2.379\ c^2)$ for 0.4 M solution

$D = 10^{-5} (2.582 - 1.769\ c + 0.752\ c^2)$ for 0.6 M solution

$D = 10^{-5} (2.351 + 3.465\ c - 6.635\ c^2)$ for 0.8 M solution

where D = diffusivity, and c = concentration

These equations were obtained by the method of least squares.

5.7 Comparison of Diffusivities in Aqueous and Organic Phases.

The comparison between diffusivities as shown in Table 4.2 and Table 4.3 indicated that the diffusivity values in the aqueous phase was

higher than that in the organic phase. This could be explained that:1) the molecules of TBP and kerosene were larger than that of HNO_3, 2) thorium and nitrate ion were probably formed complex with TBP molecule as the following equation:

$$Th^{4+} + 4\ NO_3^- + TBP \longrightarrow Th(NO_3)_4\ \ TBP$$

A similar system with uranium instead of thorium were reported by Baumgartner and Finsterwalder[25] to form complex molecules. The complex with larger molecular sizes lowered the diffusivity value.

5.8 Conclusions

1. A low cost, simple capillary cell was designed to investigate the diffusion coefficient. The capillary cells were constructed and calibrated with KCl solution. A computer simulation of the diffusion process with out stirring provided a procedure for the estimation of diffusion coefficients from the residual amount in the capillary at any time was used. The accuracy of this method was within about 89 %.

2. The diffusion coefficients of $Th(NO_3)_4$ in 4 N HNO_3 from 10.5°c to 30.5°c and 0.05 M to 0.8 M were determined.

3. The diffusion coefficient of 0.8 M $Th(NO_3)_4$ in TBP - Kerosene was also determined.

4. The diffusivity of $Th(NO_3)_4$ increased as the temperature increased according to the equation $D = D_o e^{-E/T}$, but decreased as the concentration increased. E was dependent on concentration.

5. The diffusivity of $Th(HO_3)_4$ in 4 N HNO_3 phase was higher than that in TBP - Kerosene phase.