DETERMINATION OF SORET COEFFICIENTS FOR ETHANOL-WATER SYSTEM

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SUMMARY

The Soret coefficients were determined for the binary liquid system, ethanol-water, in connection with a graduate research project carried on by Mr. Edward Von Halle.

In this project initial solutions of 18.9%, 49.0%, and 92.7% ethanol by weight were investigated using a diffusion chamber placed between hot and cold copper walls. The chamber was divided into equal compartments by a stretched piece of cellophane. At the end of various periods of time refractive index measurements were made on the solutions from both the hot and cold compartments for the purpose of determining the corresponding concentrations. Thermocouple measurements were also made at the hot and cold copper walls.

The Soret coefficients for each of the initial solutions were calculated using two equations and average values of the resulting concentrations of solution in both the hot and cold compartments and the average values of the temperature differences between the hot and cold walls. The average Soret coefficients were -0.001663, 0.00113, and -0.01070 for the 18.9%, 49.0%, and 92.7% initial solutions respectively. These Soret coefficients along with the average temperature differences, the distances between the hot and cold walls, and the calculated constants, β_1, β_2, A_1, A_2, a_1, and a_2 were used to derive equations for the cold compartment in terms of the time for the three runs.

Plots were made of the cold compartment concentration versus time. Curves for the hot compartment concentration were constructed symetrically about the horizontal lines representing the initial concentrations.

Points representing the concentrations obtained experimentally were shown on the graphs for comparison with the calculated curves.

It was concluded that the measured and calculated concentrations were inconsistent. Possible sources of error involve the possibility of the evaporation of a greater portion of the more volatile constituent, ethanol, than water, contamination of the solution within the compartments with foreign matter, and the leaking of some of the solution in the compartments.

Further experimentation is recommended with greater precautions taken to eliminate the "pit falls" of the present work.

INTRODUCTION

As part of a graduate research project, which is being carried on in the Chemical Engineering laboratory at the University of Tennessee by Mr. Edward Von Halle (6), it was necessary to carry out experimental work in order to obtain data for determining the Soret coefficients as a function of concentration for the system, ethanol-water.

When a solution is maintained for a period of time in a temperature gradient, a difference in concentration will be set up between the hot and cold boundaries of the chamber containing the solution. Previous work connected with this phenomenon, which is known as the Soret effect, was carried out first by Ludwig (3) in 1856. Other experimental investigators of the Soret effect were Soret (4), Van't Hoff (5), and Chapman (1).

THEORY

The Soret coefficient, which is the ratio of the coefficient of thermal diffusion to the coefficient of molecular diffusion, can be calculated from experimental data obtained from a binary liquid system. The apparatus consists of a diffusion chamber placed between hot and cold walls. The chamber is divided into two equal compartments by a diaphram of cellophane. For calculating the Soret coefficient, one of the following equations developed by Von Halle (6) may be used depending on the concentration of the solution placed in the diffusion chamber:

$$C_H - C_c = \frac{D'}{D}\left(\frac{\Delta T}{2}\right) C_i (1 - C_i) \qquad (1)$$

$$\frac{D'}{D}\left(\frac{\Delta T}{2}\right) = \ln\left(\frac{C_H}{1-C_H}\right)\left(\frac{1-C_c}{C_c}\right) \qquad (2)$$

Where $\frac{D'}{D}$ = Soret coefficient

D' = Coefficient of thermal diffusion $\frac{\text{sq.cm.}}{\text{hr.}}$

D = Coefficient of molecular diffusion $\frac{\text{sq.cm.}}{\text{hr.}}$

C_H = Average concentration on hot side of cellophane at steady state conditions (wt. fraction ethanol)

C_c = Average concentration on cold side of cellophane at steady state conditions (wt. fraction ethanol)

C_i = Initial concentration of solution in chamber (wt. fraction ethanol)

ΔT = Temperature difference between hot wall and cold wall ($^{\circ}F$)

If the concentration of the solution placed in the diffusion chamber is close to 50% ethanol by weight, either equation may be used for calculating the Soret coefficient. However, the further the value of the concentration of the initial solution is from 50% ethanol by weight, the greater is the difference in the values of the Soret coefficients obtained by the two equations. It has been found that for a low initial concentration greater accuracy can be obtained using equation (1), while for a high initial concentration it is more accurate to use equation (2).

The average concentration in the cold side at any time after the temperature gradient is set up on the initial solution, can be calculated by the following equation:

$$C_{c(t)} = C_i - \frac{D'}{D}\frac{\Delta T}{2R} C_i(1-C_i)\left[\frac{R}{4} + \frac{2}{R}\sum_{m=1}^{\infty} A_m \frac{\sin \beta_m\left(\frac{R}{2}\right)}{\beta_m}\, e^{-a_m t}\right] \quad (3)$$

Where $C_{c(t)}$ = Average concentration in the cold compartment at any time, t (wt. fraction ethanol)

R = Distance between hot and cold walls (cm.)

t = Time since solution was placed in compartments (hrs.)

The constants, β_m, A_m, and a_m in equation (3) can be calculated by the following relationships:

$$\tan \beta_m\left(\frac{R}{2}\right) = \frac{2\Theta}{\beta_m \delta} \quad (4)$$

$$A_m = \frac{1-\Theta-\cos \beta_m\left(\frac{R}{2}\right) - \frac{2\Theta}{\beta_m \delta}\sin \beta_m\left(\frac{R}{2}\right)}{\beta_m^2\left[\frac{\Theta R + (1-\Theta)\delta}{2\delta\beta_m}\sin \beta_m\left(\frac{R}{2}\right) + \frac{R}{4}\cos \beta_m\left(\frac{R}{2}\right)\right]} \quad (5)$$

$$a_m = \beta_m^2 D \quad (6)$$

Where Θ = Free area cellophane, 0.15 cm.

δ = Thickness of cellophane, 0.008 cm.

For calculating concentrations in the cold compartment at values of t greater than four hours, only the first root, β_1 , of equation (4) is needed. For values of t less than four hours greater accuracy is obtained if the second root, β_2 , of equation (4) is also used. The values for β_1 and β_2 are found by solving equation (4) by a trial and error procedure. Then values for A_1 , A_2 , a_1 , and a_2 can be calculated from β_1 and β_2 using equations (5) and (6).

As steady state conditions are approached, the following term in equation (3) approaches zero:

$$\frac{2}{R}\sum_{n=1}^{\infty} A_n \frac{\sin \beta_n\left(\frac{R}{2}\right)}{\beta_n} e^{-a_n t}$$

The resulting equation for finding the concentration in the cold compartment at steady state conditions is as follows:

$$C_c = C_i - \frac{D'}{D}\frac{\Delta T}{\partial R} C_i(1-C_i) \qquad (7)$$

The average concentrations at any time in the hot compartment are found graphically by constructing a curve symetrically about the horizontal line representing the initial concentration. If the Soret coefficient is positive the lower curve will be for $C_{c(t)}$ and the upper curve for $C_{H(t)}$. If the Soret coefficient is negative the reverse will be true.

EXPERIMENTAL APPARATUS

The experimental apparatus consists of a rectangular cell placed between hot and cold metal walls. The cell is divided into two parts, the upper and lower compartments. The hot and cold walls are constructed of copper in order for there to be good heat transfer, and the material making up the sides of the compartments is Cycleweld Resin, C-17, (Chrysler Corporation).

The hot and cold temperatures of the copper walls of the compartments are obtained by passing hot and cold water through holes in the upper and lower copper sections of the cell. An electric heater is used to heat the hot water, and a circulating pump is used for pumping the hot and cold water through the copper sections of the cell.

The disassembled upper and lower sections of the cell are shown in Figures 1 and 2. It can be seen in Figure 1 that the upper compartment, which is the hot compartment, contains a piece of wire screen, which covers the open end of the Cycleweld Resin, C-17. The purpose of this wire screen is to prevent the cellophane, which is stretched between the two compartments when assembled, from being pressed against the copper wall of the upper compartment by a pressure set up within the ethanol-water solution. During previous experimentation with this type of diffusion cell it was found that a thermal osmotic pressure difference is set up by the difference in temperature in the chamber causing a force in the direction of the hot wall. An attempt was made to measure the variation of pressure with time, but accurate results could not be obtained because of a loss of solution from the system. Such a loss of

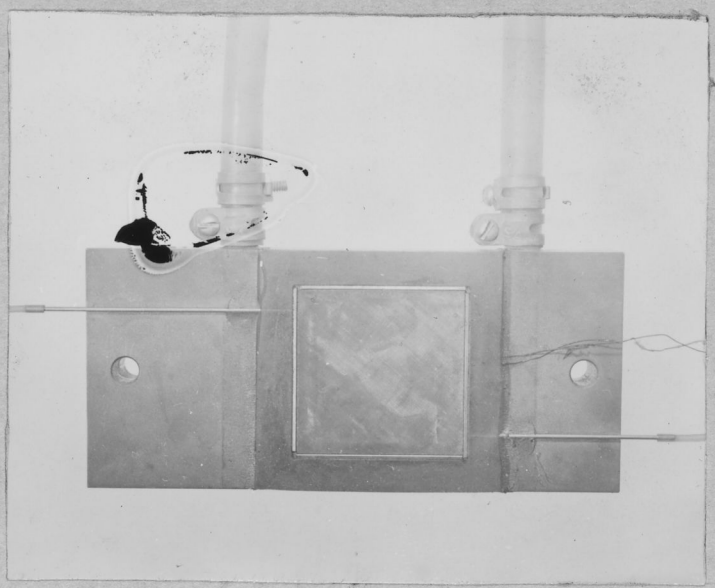


FIGURE 1

Upper Section of Diffusion Cell

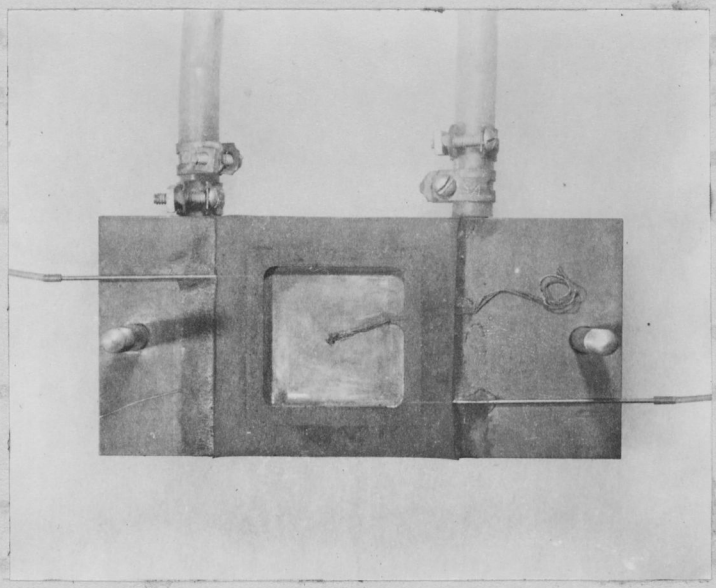


FIGURE 2

Lower Section of Diffusion Cell

solution could have resulted from either evaporation or leaks in the equipment. In trying to eliminate possible leaks, the connections between the cell and the measuring apparatus were changed several times, but the loss of solution could not be eliminated using materials that were available for the connections.

The inlets and outlets to the upper and lower compartments consist of rubber tubing connected to steel tubing. Larger rubber tubing, connected to the copper sections by morman clamps, is used for transferring the heating and cooling water to and from the cavities in the copper sections.

In order to obtain the temperatures at the hot and cold walls, copper-constantan thermocouple wires are connected to the hot and cold walls.

In Figure 3 the diffusion cell is shown assembled with the cellophane stretched between the two compartments and the inlets and outlets to the compartments clamped to prevent leakages. As an additional guard against leakages, the open ends of the Cycleweld Resin, C-17, are coated with a thin layer of vacuum grease before assembling the cell.

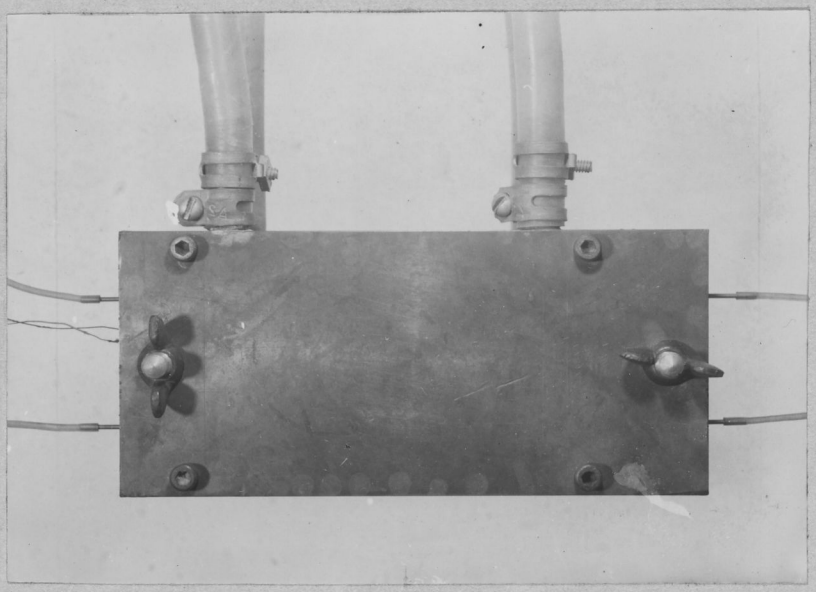


FIGURE 3

Assembled Diffusion Cell

PROCEDURE

Three runs were made using initial solutions of 18.9%, 49.0%, and 92.7% ethanol by weight. Using each of these initial solutions, the cell was filled several times, with the heating and cooling water being turned on each time, and the solution was allowed to remain in the cell for known periods of time under the influence of the temperature gradient caused by the hot and cold copper walls. At the end of each period of time for each initial concentration, the upper and lower compartments were emptied and the refractive index of the solution from each compartment was measured with an Abbi refractometer. Thermocouple readings were also made at both the hot and cold walls.

The cell was filled each time by tilting the cell at an angle and allowing the initial solution to flow into the inlet tubing at the lower end of each compartment of the cell from a measuring flask clamped at a level above the cell. Each time the lower compartment was filled first. The filling of each compartment was not stopped until the solution began to come out of the exit tubing at the inclined end of the compartment being filled in order to avoid bubbles in the solution in the compartment.

During emptying, the compartments were tilted again in order for the solution to flow out. The solution from each compartment was emptied completely into separate containers so that the measured refractive index for the solution from each compartment would be the average refractive index for the solution from that compartment.

Before filling the diffusion cell each time, the cell was disassembled and a new piece of cellophane was stretched between the two compartments

as the bolts were tightened. Each piece of cellophane had been allowed to remain in a tray of distilled water for at least a day and a tray of the initial solution for at least two hours before being used in the cell.

The recorded refractive indices were converted to concentration units of weight fraction ethanol by using the plot of refractive index versus concentration from Figure 7 in the appendix.

The thermocouple readings were converted to temperatures by using Table VI in the appendix and interpolating. For the positive thermocouple readings the differences between the room temperatures and 32° F. were added to the temperatures corresponding to the millivolt values in Table VI. For the negative thermocouple readings the sums of the room temperatures and 32° F. were first obtained. The temperatures corresponding to the millivolt values in Table VI were subtracted from these sums to get the actual temperatures.

For each of the initial solutions the Soret coefficients were calculated from the resulting concentrations for periods of time greater than twenty hours, because it was assumed that steady state conditions were reached after about twenty hours. Equation (1) and equation (2) were used for calculating the Soret coefficients, with C_c, C_H, and ΔT obtained by averaging the experimental values for periods of time greater than twenty hours. Equation (1) was used for Runs I and II, with equation (2) being used for Run III. It was found after calculating the Soret coefficients for all three runs using both equations, that equation (1) produced more accurate results for low initial concentrations, and equation (2) produced more accurate results for high initial concentrations. However, it was found that both equations gave a Soret coefficient of about

the same value for the initial concentration of 49% ethanol by weight for Run II.

Using the resulting Soret coefficients, equation (3) was used for obtaining the average concentration in the cold compartment, C_C, in terms of the time, t, for each of the three runs. After obtaining these relationships, the curves were plotted. The curves for the average concentrations in the hot compartment were obtained by constructing symetrical curves about the horizontal lines representing the initial concentrations. These curves give a good idea of how the concentrations in the hot and cold compartments should have changed after different periods of time. Points corresponding to the experimental data are also shown on the graphs for comparison with the calculated curves.

RESULTS

The resulting concentrations and temperatures for Runs I, II, and III are tabulated in Tables I, II, and III. The Soret coefficients and constants used in deriving the three cold compartment concentration equations, are tabulated in Tables IV and V. The cold compartment concentration equations are as follows for Runs I, II, and III respectively:

$$C_{C(t)} = 0.1919 - 0.00306e^{-0.2033t} + 0.0001356e^{-1.825t} \quad (8)$$

$$C_{C(t)} = 0.4868 + 0.00336e^{-0.2033t} - 0.000149e^{-1.825t} \quad (9)$$

$$C_{C(t)} = 0.9354 - 0.00879e^{-0.315t} + 0.0004465e^{-2.81t} \quad (10)$$

The resulting concentration curves, including points for the experimental concentrations are plotted in Figures 4, 5, and 6. In the appendix the original data are shown in Tables VII, VIII, and IX, and the sample calculations on pages 36 - 39.

TABLE I

Concentration Results for Run I

Initial Concentration = 18.9% ethanol by weight

Measurement Number	Time of Run (Hours)	Concentration of Hot Compartment Solution (wt. fraction ethanol)	Concentration of Cold Compartment Solution (wt. fraction ethanol)	Hot Wall Temperature (°F.)	Cold Wall Temperature (°F.)
1	43.083	0.174	0.184	152.10	62.53
2	23.917	0.160	0.168	155.57	62.12
3	23.917	0.177	0.193	155.07	64.32
4	47.000	0.171	0.189	152.03	64.28
5	66.250	0.152	0.158	156.67	63.10

TABLE II

Concentration Results for Run II

Initial Concentration = 49.0% ethanol by weight

Measurement Number	Time of Run(Hours)	Concentration of Hot Compartment Solution (wt.fraction ethanol)	Concentration of Cold Compartment Solution (wt.fraction ethanol)	Hot Wall Temperature(^{o}F.)	Cold Wall Temperature(^{o}F.)
1	47.92	0.490	0.480	102.45	57.14
2	22.92	0.490	0.485	145.74	58.04
3	5.16	0.455	0.497	149.01	58.80
4	42.75	0.507	0.483	151.42	62.95
5	23.58	0.497	0.485	155.33	63.48
6	96.00	0.907	0.904		

TABLE III

Concentration Results for Run III

Initial Concentration = 92.7% ethanol by weight

Measurement Number	Time of Run(Hours)	Concentration of Hot Compartment Solution (wt. fraction ethanol)	Concentration of Cold Compartment Solution (wt. fraction ethanol)	Hot Wall Temperature(°F.)	Cold Wall Temperature(°F.)
1	43.75	0.808	0.890	102.32	57.31
2	94.25	0.808	0.890	154.60	58.63
3	22.58	0.907	0.927	142.35	58.48
4	4.92	0.927	0.927	152.08	59.76
5	22.67	0.917	0.927	151.13	58.90
6	96.00	0.907	0.904		

TABLE IV

Calculated Soret Coefficients

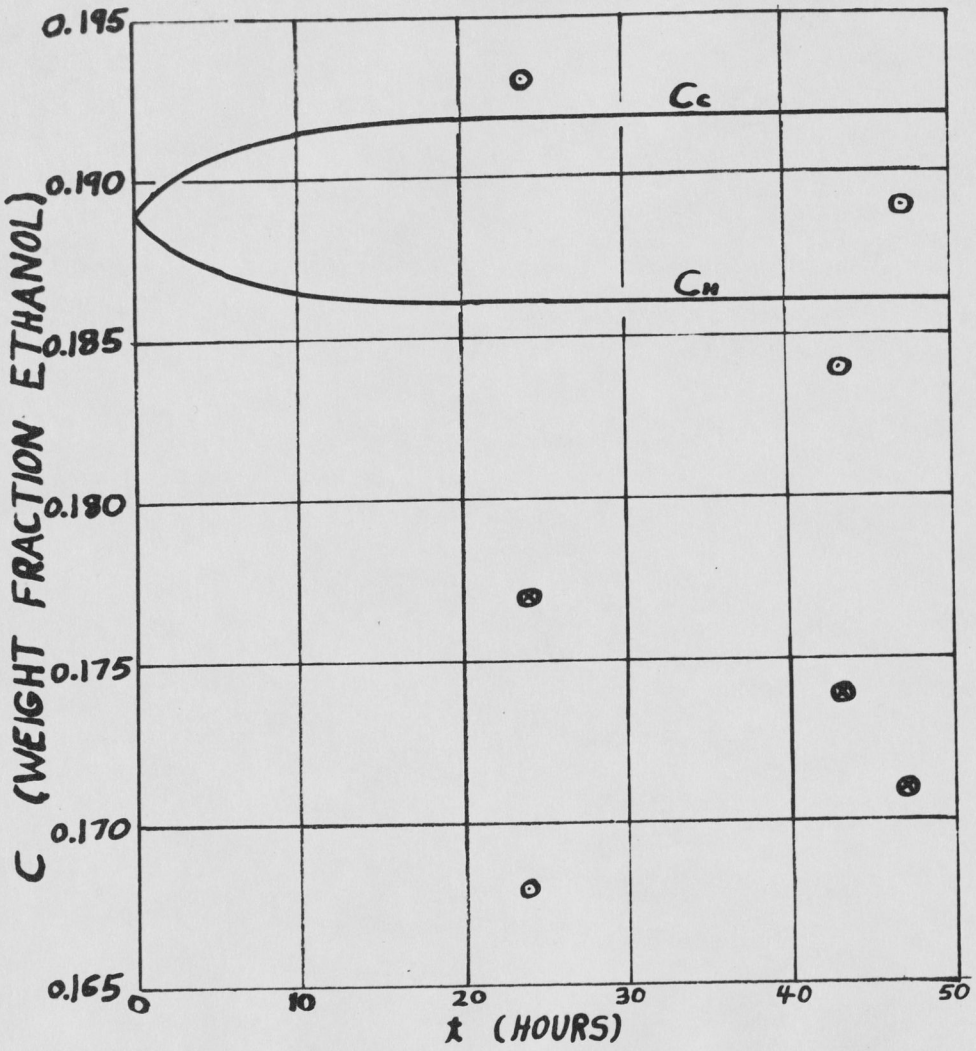
Run	Initial Concentration (wt.fraction ethanol)	Distance Between Hot and Cold Walls (cm.)	Soret Coefficient as Calculated from Equation(1)	Soret Coefficient as Calculated from Equation(2)	Soret Coefficient Used in Calculating Cc(t)
I	0.189	1.27	-0.001663	-0.0656	-0.001663
II	0.490	1.27	0.001137	0.00118	0.00113
III	0.927	1.01	-0.1597	-0.0107	-0.01070

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TABLE V

Calculated Constants

Run	β_1	β_2	A_1	A_2	a_1	a_2
I	2.375	7.12	-0.509	-0.06860	0.2033	1.825
II	2.375	7.12	-0.509	-0.06860	0.2033	1.825
III	2.957	8.87	-0.405	-0.06325	0.3150	2.831



LEGEND

⊗ EXPERIMENTAL HOT COMPARTMENT CONCENTRATIONS

⊙ EXPERIMENTAL COLD COMPARTMENT CONCENTRATIONS

C_H CALCULATED HOT COMPARTMENT CONCENTRATION

C_c CALCULATED COLD COMPARTMENT CONCENTRATION

FIGURE 4: CONCENTRATION CURVES FOR RUN I

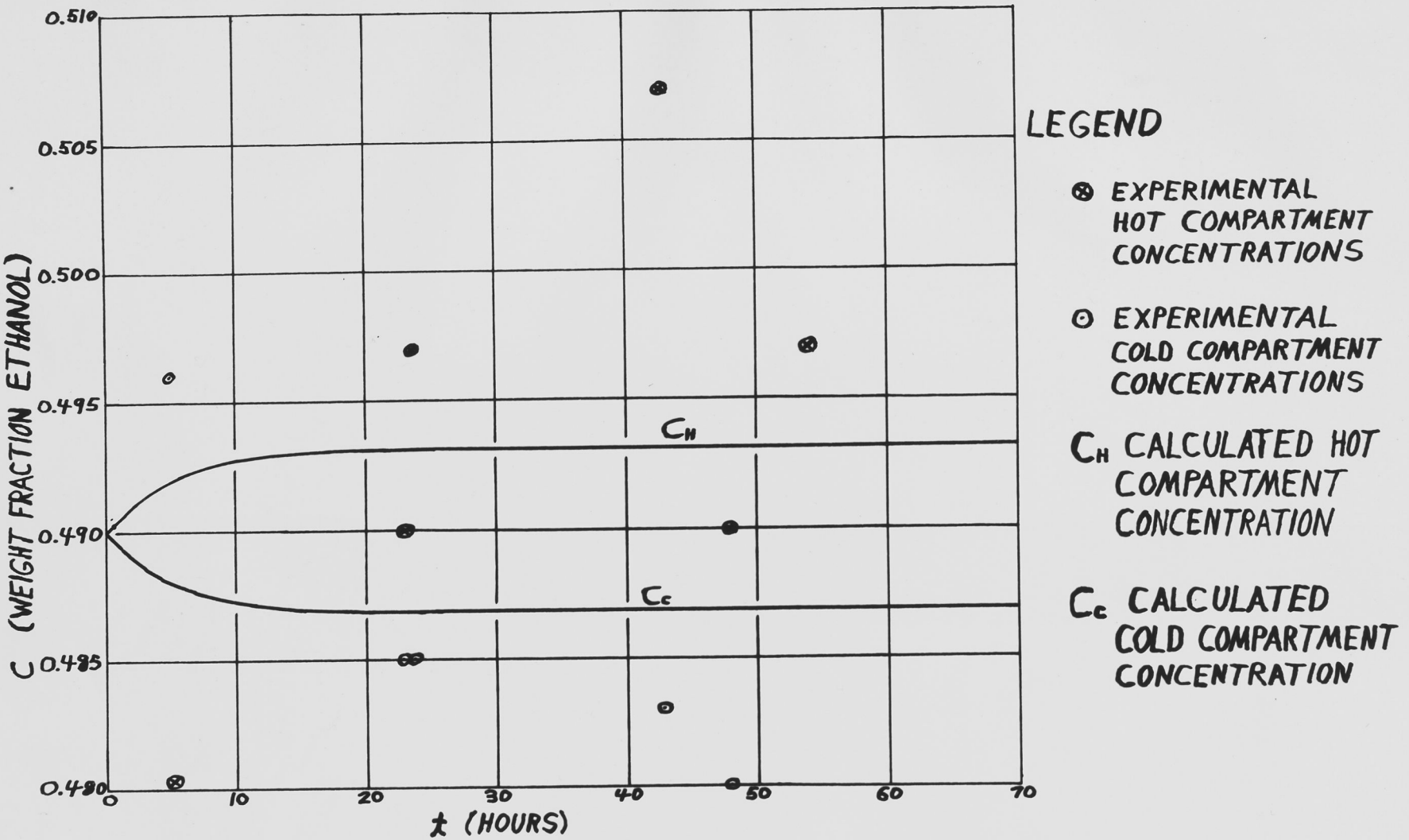


FIGURE 5: CONCENTRATION CURVES FOR RUN II

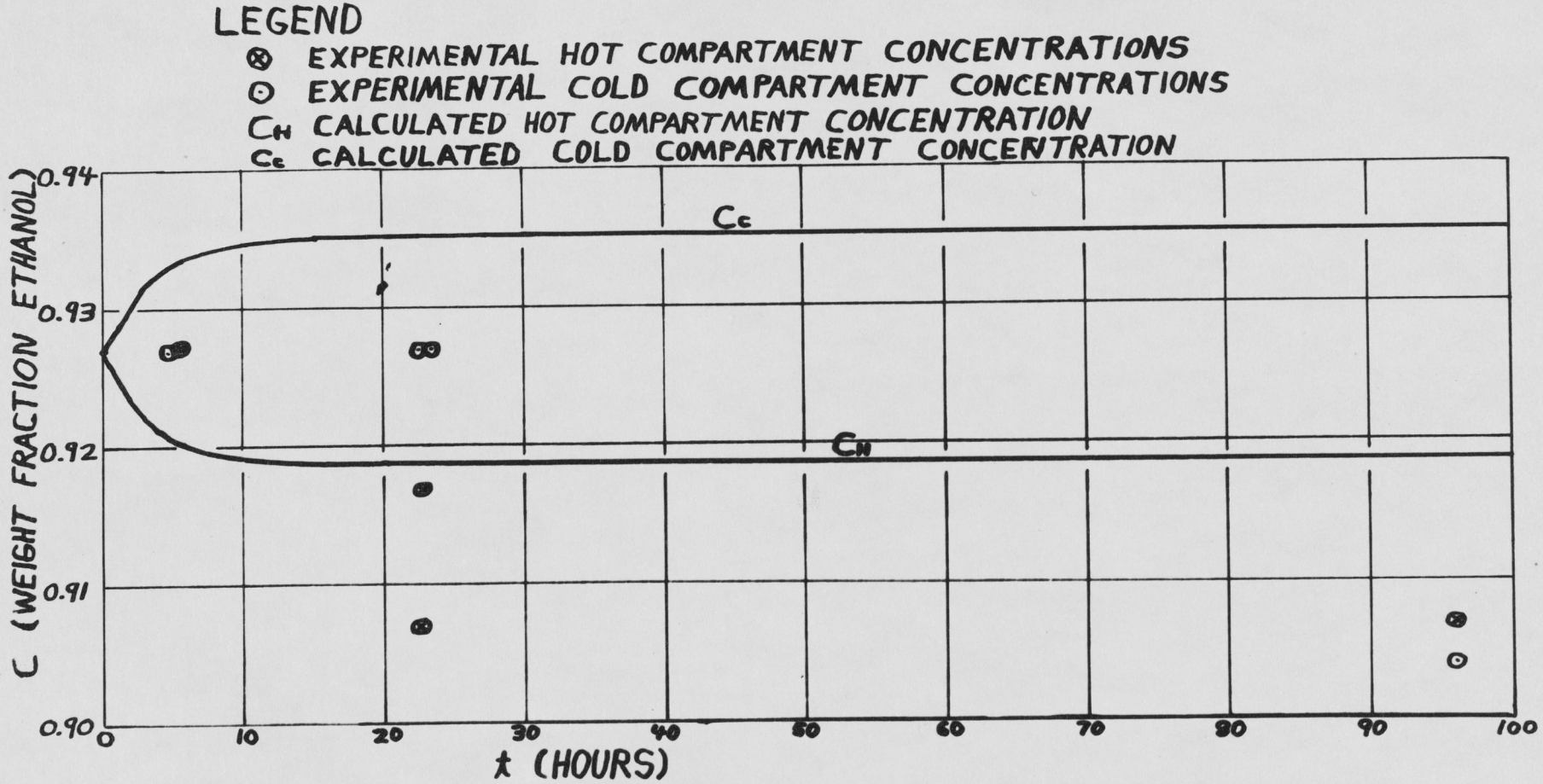


FIGURE 6: CONCENTRATION CURVES FOR RUN III

DISCUSSION OF RESULTS

From Figures 4, 5, and 6 it can be seen that the concentrations obtained experimentally are very inaccurate. Accurate material balances could not be obtained for any of the three initial solutions. In several cases the concentrations in the two compartments were both less than the initial concentration after a certain period of time had passed. This was true at $t = 23.92$ and $t = 47.00$ in Figure 4 and at $t = 43.75$, $t = 94.25$, and $t = 96.00$ in Figure 6. At $t = 49.00$ in Figure 5 the experimental values showed concentration increases in both compartments.

The inaccurate concentrations obtained experimentally could have been caused by a number of conditions. A possible source of error could have been the evaporation of a portion of the more volatile constituent, ethanol, during the time in the cell. Such unequal evaporation of the solution would lower the concentration of the solution in the cell causing the measured refractive indices to be in error. The refractive indices could also have been influenced by any foreign material from the surroundings that might have contaminated the solutions from the two compartments. Because of the possible contamination with foreign materials or the possible evaporation of greater portions of ethanol than water, the initial solution could have changed in concentration from the time it was prepared to the time of filling the cell. To avoid possibilities of errors the initial solutions were checked before filling each time to see if the refractive indices had changed. Several times it was necessary to

prepare new initial solutions because of changes in the refractive indices. The possibility of leaks in the cell was also present throughout the period of experimental work. To avoid some possibilities of leaks the Cycleweld Resin, C-17, was coated with vacuum grease each time before inserting the cellophane and tightening the bolts. Leakages could cause air spaces in the compartments. Such air spaces would interfere with the rate of diffusion within the cell.

A positive Soret coefficient was obtained for the 49.0% ethanol initial solution with negative Soret coefficients being obtained for the 18.9% and the 92.7% ethanol initial solutions. When the higher experimental concentrations were obtained for the solution from the hot compartment, a positive Soret coefficient resulted as in Run II. When the higher experimental concentrations were obtained for the solution from the cold compartment, a negative Soret coefficient resulted as was the case in Runs I and III. The calculated Soret coefficients that were used in the calculation of Cc in terms of t were -0.001663, 0.00113, and -0.0107 for Runs I, II, and III respectively. Equation (1) was used for calculating the Soret coefficients for Runs I and II, and equation (2) was used for Run III, when an initial concentration of 92.7% ethanol by weight was used. If the Soret coefficient, -0.1597, as calculated using equation (1) had been used for Run III in obtaining the relationship for Cc in terms of t, the upper curve, representing Cc, would have extended above 100% ethanol on the graph before reaching the steady state region.

It is probable that there is considerable error in the values obtained for the Soret coefficients, since they were calculated from averages of

some of the experimental steady state concentrations, which were quite inaccurate. Errors in the Soret coefficients would cause the derived plots of C_C and C_H versus t to be in error. However, since average values of the hot and cold compartment concentrations were used in calculating the Soret coefficients, the resulting Soret coefficients and derived curves are the best that can be obtained using such inaccurate experimental data.

CONCLUSIONS AND RECOMMENDATIONS

Although significant conclusions cannot be drawn from the results of this investigation because of the scattering of experimental concentrations in Figures 4, 5, and 6, certain trends are shown by the experimental concentrations. For initial concentrations of 18.9% and 92.7% ethanol the hot compartment concentrations generally decreased with time, and for an initial concentration of 49.0% ethanol, the cold compartment concentrations generally decreased with time. No general increases or decreases are recognized for the cold compartment concentrations for the initial solutions of 18.9% and 92.7% ethanol or for the hot compartment concentrations for the initial solution of 49.0% ethanol.

Because of the scattering of points representing experimental concentrations, and the failure of the experimental points from lying in the vicinity of the calculated concentration curves, a further investigation of the Soret effect is necessary for clarifying the situation. In carrying out an additional investigation, improvements in the equipment should be made in order to reduce errors caused by leakages, contamination with foreign materials, and the unequal evaporation of the binary constituents.

LIST OF NOMENCLATURE

a_n = Empirical constant ($n = 1, 2, 3, \ldots, \infty$)

A_n = Empirical constant ($n = 1, 2, 3, \ldots, \infty$)

C_C = Average concentration in cold compartment of diffusion cell (wt. fraction ethanol)

C_i = Initial concentration or initial concentration of solution in cell (wt. fraction ethanol)

C_H = Average concentration in hot compartment of diffusion cell (wt. fraction ethanol)

D = Coefficient of molecular diffusion $\left(\frac{\text{sq. cm.}}{\text{hr.}}\right)$

$\frac{D'}{D}$ = Soret coefficient (dimensionless)

R = Distance between hot and cold walls (cm.)

t = Time for solution in cell (hours)

T = Temperature ($^{\circ}F$)

ΔT = Temperature difference between hot and cold copper walls as obtained from thermocouple measurements ($^{\circ}F$)

β_n = Empirical constant ($n = 1, 2, 3, \ldots, \infty$)

δ = Thickness of cellophane (cm.)

Θ = Free area of cellophane (sq. cm.)

REFERENCES

(1) Chapman, Transactions of the Royal Society (London) 216A, 279 (1916).

(2) Chipman, J., "The Soret Effect", Journal of the American Chemical Society 48 2577 (1926).

(3) Ludwig, Berichte der Wiener Akademie der Wissenschaften 20, 539 (1856).

(4) Soret, Achieves des Sciences Physiques et Natuelles 2, 48 (1879).

(5) Van't Hoff, Zeitschrift fun Physikalische Chemie 1, 487 (1887).

(6) Von Halle, Edward, Private communication.

APPENDIX

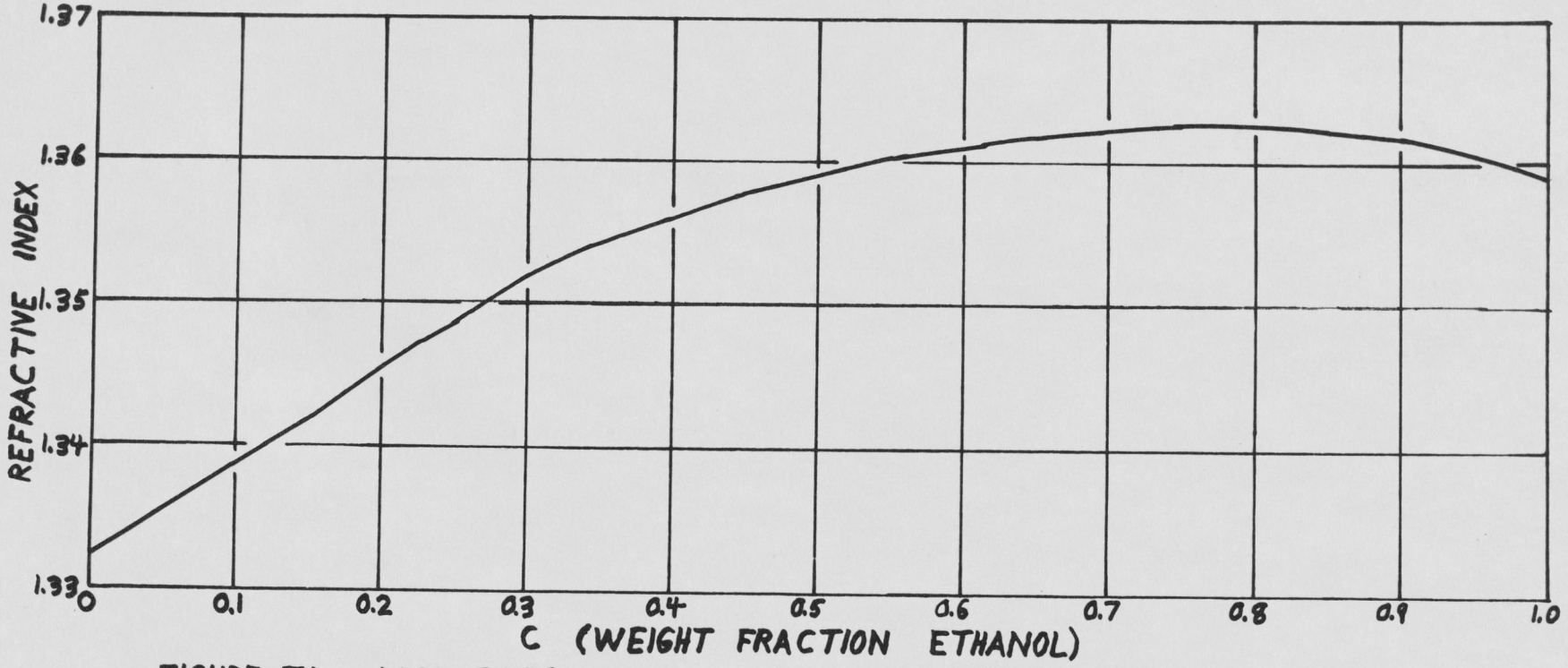


FIGURE 7: ABBI REFRACTOMETER CALIBRATION CURVE FOR ETHANOL–WATER SYSTEM

TABLE VI

TEMPERATURES FOR THERMOCOUPLE READINGS

Thermocouple Reading (Millivolts)	Temperature (°F)
0	32.00
100	36.66
200	41.29
300	45.90
400	50.49
500	55.04
600	59.58
700	64.09
800	68.58
900	73.04
1000	77.49
1100	81.90
1200	86.27
1300	90.63
1400	94.96
1500	99.28
1600	103.59
1700	107.87
1800	112.12

TABLE VII

Original Data for Run I

Initial Concentration = 18.9% ethanol by weight

Measurement No.	Time of Run(Hrs.)	Refractive Index of Hot Compartment Solution	Refractive Index of Cold Compartment Solution	Hot Wall Thermocouple Reading (millivolts)	Cold Wall Thermocouple Reading (millivolts)	Room Temperature (°F.)
1	43.083	1.3435	1.3443	1301.9	-664.2	93.0
2	23.917	1.3425	1.3431	1390.9	-673.1	93.0
3	23.917	1.3438	1.3450	1437.2	-569.3	90.5
4	47.000	1.3433	1.3447	1657.0	-296.1	78.0
5	66.250	1.3438	1.3446	1462.7	-607.0	91.0

TABLE VIII

Original Data for Run II

Initial Concentration = 49.0% ethanol by weight

Measurement No.	Time of Run(Hrs.)	Refractive Index of Hot Compartment Solution	Refractive Index of Cold Compartment Solution	Hot Wall Thermocouple Reading (millivolts)	Cold Wall Thermocouple Reading (millivolts)	Room Temperature (°F.)
1	47.92	1.3588	1.3585	443.1	-540.2	82.0
2	22.92	1.3588	1.3587	1395.0	-542.4	83.0
3	5.16	1.3578	1.3590	1517.0	-525.5	83.0
4	42.75	1.3593	1.3586	1295.2	-654.8	93.0
5	23.58	1.3590	1.3587	1394.7	-643.0	93.0

TABLE IX

Original Data for Run III

Initial Concentration = 92.7% ethanol by weight

Measurement No.	Time of Run(Hrs.)	Refractive Index of Hot Compartment Solution	Refractive Index of Cold Compartment Solution	Hot Wall Thermocouple Reading (millivolts)	Cold Wall Thermocouple Reading (millivolts)	Room Temperature (°F.)
1	43.75	1.3627	1.3620	440.1	-536.4	82.0
2	94.25	1.3627	1.3620	1600.2	-529.3	83.0
3	22.58	1.3617	1.3613	1316.7	-532.6	83.0
4	4.92	1.3613	1.3613	1495.3	-504.5	83.0
5	22.67	1.3615	1.3613	1729.6	-326.2	74.0
6	96.00	1.3617	1.3618			

Sample calculations are as follows:

Run number = I

Measurement number = 1

Time of solution in cell = 43.08 hours (original data)

Refractive index of hot compartment solution = 1.3435 (original data)

Concentration of hot compartment solution (wt. fraction ethanol) = 0.174 (obtained from curve in Figure 7)

Refractive index of cold compartment solution = 1.3443 (original data)

Concentration of cold compartment solution (wt. fraction ethanol) = 0.184 (obtained from curve in Figure 7)

Room temperature = 93.0° F. (original data)

Hot wall thermocouple reading = 1301.9 millivolts (original data)

Hot wall temperature = Table VI value + (room temperature - 32)

= 91.1 + (93.0 - 32.0)

= 152.10° F.

Cold wall thermocouple reading = -664.2 millivolts (original data)

Cold wall temperature = (room temperature + 32) + Table VI temperature corresponding to -664.2 mv.

= (93.00 + 32.00) - 62.47

= 62.53° F.

Temperature difference between walls = 152.10° F. - 62.53° F.

= 89.57° F.

Calculation of Soret coefficient using values from Run I from Tables I and VII:

Average value of hot compartment concentrations at steady state (assuming steady state conditions are present when $t > 20$ hrs.) (wt. fraction ethanol) = $\frac{1}{5}$ (0.174 + 0.160 + 0.177 + 0.171 + 0.152)

= 0.1668

Average value of cold compartment concentrations at steady state ($t > 20$ hrs.) (wt. fraction ethanol) = $\frac{1}{5}$ (0.184 + 0.168 + 0.193 + 0.189 + 0.158)

= 0.1784

Average value of temperature differences between walls at steady state ($t > 20$ hrs.) $= \frac{1}{5}(89.57 + 93.45 + 90.57 + 87.75 + 93.57)$

$= 90.98^{\circ}$ F.

Initial concentration of solution in cell (wt. fraction ethanol) $= 0.189$ (original data)

Soret coefficient (dimensionless)

$$= \frac{0.1668 - 0.1784}{\frac{90.98}{2}(0.189)(1-0.189)}$$

$$= -0.001663$$

Using equation (1):

$$\frac{D'}{D} = \frac{C_H - C_C}{C_1(1-C_1)}$$

Derivation of cold compartment concentration equations using data for Run I:

Distance between hot and cold walls $= 1.27$ cm. (original data)

Constant, $\beta_1 = 2.375$

First root of equation (4):

$$\tan \beta_n \left(\frac{R}{2}\right) = \frac{2\theta}{\beta_m \delta}$$

or

$$\tan \beta_1 \left(\frac{1.27}{2}\right) = \frac{2(0.15)}{\beta_1 (0.008)}$$

Constant, β_2 = 7.12

Second root of equation (4)

Constant, A_1 = $\dfrac{1-0.15-\cos(2.375)\left(\frac{1.27}{2}\right)-\frac{2(0.15)}{(2.375)(0.008)}\sin(2.375)\left(\frac{1.27}{2}\right)}{(2.375)^2\left[\frac{0.15(1.27)+0.85(0.008)}{2(0.008)(2.375)}\sin(2.375)\left(\frac{1.27}{2}\right)\frac{1.27}{4}+\frac{1.27}{4}\cos(2.375)\left(\frac{1.27}{2}\right)\right]}$

= -0.509

From equation (5): $A_n = \dfrac{1-\theta-\cos\beta_m\left(\frac{R}{2}\right)-\frac{2\theta}{\beta_m\delta}\sin\beta_m\left(\frac{R}{2}\right)}{\beta_m^2\left[\frac{\theta R+(1-\theta)\delta}{2\delta\beta_m}\sin\beta_m\left(\frac{R}{2}\right)+\frac{R}{4}\cos\beta_m\left(\frac{R}{2}\right)\right]}$

with (n = 1)

Constant, A_2 = -0.0686

From equation (5) with n = 2

Constant, a_1 = $(2.375)^2$ (0.036) = 0.2033

From equation (6): $a_n = \beta_n^2 D$ (n = 1)

Constant, a_2 = 1.825

From equation (6) with n = 2

Cold compartment concentration equation:

$C_c = 0.1919 - 0.00306e^{-0.2033t} + 0.0001356e^{-1.825t}$

From equation (3):

$$C_{c(t)} = C_i - \frac{D'}{D}\frac{\Delta T}{2R}C_i(1-C_i)\left\{\frac{R}{4}+\frac{2}{R}\left[A_1\frac{\sin\beta_1\left(\frac{R}{2}\right)}{\beta_1}e^{-a_1t}+A_2\frac{\sin\beta_2\left(\frac{R}{2}\right)}{\beta_2}e^{-a_2t}\right]\right\}$$

APPROVAL

The foregoing thesis is hereby approved as a creditable study of an engineering subject, carried out and presented in a manner sufficiently satisfactory to warrant its acceptance as a prerequisite to the degree for which it has been submitted. It is to be understood that by his approval the undersigned does not necessarily endorse or approve any statement made, opinions expressed, or conclusions drawn therein, but approves the project report only for the purpose for which it is submitted.

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