UNSTEADY-STATE MACROSCOPIC BALANCES

In this chapter we will consider unsteady-state transfer processes between phases by assuming no gradients within each phase. Since the dependent variables, such as temperature and concentration, are considered uniform within a given phase, the resulting macroscopic balances are ordinary differential equations in time.

The basic steps in the development of unsteady macroscopic balances are similar to those for steady-state balances given in Chapter 6. These can be briefly summarized as follows:

- Define your system.
- If possible, draw a simple sketch.
- List the assumptions.
- Write down the inventory rate equation for each of the basic concepts relevant to the problem at hand.
- Use engineering correlations to evaluate the transfer coefficients.
- Write down the initial conditions: the number of initial conditions must be equal to the sum of the order of differential equations written for the system.
- Solve the ordinary differential equations.

7.1 APPROXIMATIONS USED IN MODELING OF UNSTEADY-STATE PROCESSES

7.1.1 Pseudo-Steady-State Approximation

As stated in Chapter 1, the general inventory rate equation can be expressed in the form

$$\begin{pmatrix}\text{Rate of}\\ \text{input}\end{pmatrix} - \begin{pmatrix}\text{Rate of}\\ \text{output}\end{pmatrix} + \begin{pmatrix}\text{Rate of}\\ \text{generation}\end{pmatrix} = \begin{pmatrix}\text{Rate of}\\ \text{accumulation}\end{pmatrix} \tag{7.1-1}$$

Remember that the molecular and convective fluxes constitute the input and output terms. Among the terms appearing on the left-hand side of Eq. (7.1-1), molecular transport is the slowest process. Therefore, in a given unsteady-state process, the term on the right-hand side of Eq. (7.1-1) may be considered negligible if

$$\begin{pmatrix}\text{Rate of}\\ \text{molecular transport}\end{pmatrix} \gg \begin{pmatrix}\text{Rate of}\\ \text{accumulation}\end{pmatrix} \tag{7.1-2}$$

or,

$$(\text{Diffusivity})\begin{pmatrix}\text{Gradient of}\\ \text{Quantity/Volume}\end{pmatrix}(\text{Area}) \gg \frac{\text{Difference in quantity}}{\text{Characteristic time}} \tag{7.1-3}$$

Note that the "Gradient of Quantity/Volume" is expressed in the form

$$\text{Gradient of Quantity/Volume} = \frac{\text{Difference in Quantity/Volume}}{\text{Characteristic length}} \tag{7.1-4}$$

On the other hand, volume and area are expressed in terms of characteristic length as

$$\text{Volume} = (\text{Characteristic length})^3 \tag{7.1-5}$$

$$\text{Area} = (\text{Characteristic length})^2 \tag{7.1-6}$$

Substitution of Eqs. (7.1-4)–(7.1-6) into Eq. (7.1-3) gives

$$\boxed{\frac{(\text{Diffusivity})(\text{Characteristic time})}{(\text{Characteristic length})^2} \gg 1} \tag{7.1-7}$$

In the literature, the dimensionless term on the left-hand side of Eq. (7.1-7) is known as the *Fourier number* and designated by τ.

In engineering analysis, the neglect of the unsteady-state term is often referred to as the *pseudo-steady-state* (or *quasi-steady-state*) approximation. However, it should be noted that the pseudo-steady-state approximation is only valid if the constraint given by Eq. (7.1-7) is satisfied.

7.2 CONSERVATION OF CHEMICAL SPECIES

The conservation statement for the mass of the ith chemical species is given by

$$\begin{pmatrix}\text{Rate of mass}\\ \text{of } i \text{ in}\end{pmatrix} - \begin{pmatrix}\text{Rate of mass}\\ \text{of } i \text{ out}\end{pmatrix} + \begin{pmatrix}\text{Rate of generation}\\ \text{of mass } i\end{pmatrix} = \begin{pmatrix}\text{Rate of accumulation}\\ \text{of mass } i\end{pmatrix} \tag{7.2-1}$$

For a system with a single inlet and a single outlet stream as shown in Figure 7.1, Eq. (7.2-1) can be expressed as

$$\boxed{(\dot{m}_i)_{in} - (\dot{m}_i)_{out} \pm (\dot{m}_i)_{int} + V_{sys}\mathcal{M}_i \sum_j \alpha_{ij} r_j = \frac{d(m_i)_{sys}}{dt}} \tag{7.2-2}$$

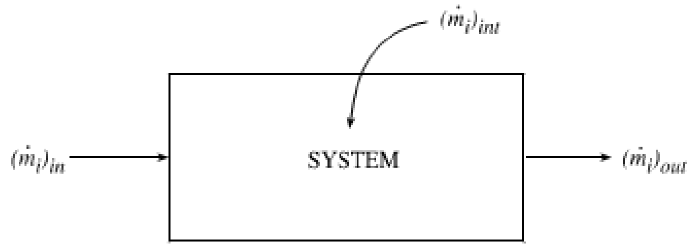


Figure 7.1. Unsteady-state flow system exchanging mass with the surroundings.

The interphase mass transfer rate, $(\dot{m}_i)_{int}$, is considered positive when mass is added to the system and is expressed by

$$(\dot{m}_i)_{int} = A_M \langle k_c \rangle (\Delta c_i)_{ch} \mathcal{M}_i \tag{7.2-3}$$

Substitution of Eq. (7.2-3) into Eq. (7.2-2) gives

$$\boxed{(\mathcal{Q}\rho_i)_{in} - (\mathcal{Q}\rho_i)_{out} \pm A_M \langle k_c \rangle (\Delta c_i)_{ch} \mathcal{M}_i + V_{sys}\mathcal{M}_i \sum_j \alpha_{ij} r_j = \frac{d(m_i)_{sys}}{dt}} \tag{7.2-4}$$

On a molar basis, Eqs. (7.2-2) and (7.2-4) take the form

$$\boxed{(\dot{n}_i)_{in} - (\dot{n}_i)_{out} \pm (\dot{n}_i)_{int} + V_{sys} \sum_j \alpha_{ij} r_j = \frac{d(n_i)_{sys}}{dt}} \tag{7.2-5}$$

and

$$\boxed{(\mathcal{Q}c_i)_{in} - (\mathcal{Q}c_i)_{out} \pm A_M \langle k_c \rangle (\Delta c_i)_{ch} + V_{sys} \sum_j \alpha_{ij} r_j = \frac{d(n_i)_{sys}}{dt}} \tag{7.2-6}$$

7.3 CONSERVATION OF TOTAL MASS

Summation of Eq. (7.2-2) over all species gives the total mass balance in the form

$$\boxed{\dot{m}_{in} - \dot{m}_{out} \pm \dot{m}_{int} = \frac{dm_{sys}}{dt}} \tag{7.3-1}$$

Note that the term $\sum_i \alpha_{ij} \mathcal{M}_i$ is zero since mass is conserved. On the other hand, summation of Eq. (7.2-5) over all species gives the total mole balance as

$$\boxed{\dot{n}_{in} - \dot{n}_{out} \pm \dot{n}_{int} + V_{sys} \sum_j \overline{\alpha}_j r_j = \frac{dn_{sys}}{dt}} \tag{7.3-2}$$

where

$$\overline{\alpha}_j = \sum_i \alpha_{ij} \tag{7.3-3}$$

The generation term in Eq. (7.3-2) is not zero because moles are not conserved. This term vanishes only when $\overline{\alpha}_j = 0$ for all values of j.

7.5 CONSERVATION OF ENERGY

The conservation statement for total energy under unsteady state conditions is given by

$$\begin{pmatrix}\text{Rate of}\\ \text{energy in}\end{pmatrix} - \begin{pmatrix}\text{Rate of}\\ \text{energy out}\end{pmatrix} = \begin{pmatrix}\text{Rate of energy}\\ \text{accumulation}\end{pmatrix} \tag{7.5-1}$$

For a system shown in Figure 7.2, following the discussion explained in Section 6.3, Eq. (7.5-1) is written as

$$\left[(\widehat{U} + \widehat{E}_K + \widehat{E}_P)\dot{m}\right]_{in} - \left[(\widehat{U} + \widehat{E}_K + \widehat{E}_P)\dot{m}\right]_{out} + \dot{Q}_{int} + \dot{W}$$
$$= \frac{d}{dt}\left[(\widehat{U} + \widehat{E}_K + \widehat{E}_P)m\right]_{sys} \tag{7.5-2}$$

Note that, contrary to the steady-state flow system, the boundaries of this system are not fixed in space. Therefore, besides shaft and flow works, work associated with the expansion or compression of the system boundaries must be included in $\dot{W}$, thus resulting in the form

$$\dot{W} = \underbrace{-P_{sys}\frac{dV_{sys}}{dt}}_{A} + \underbrace{\dot{W}_s}_{B} + \underbrace{(P\widehat{V}\dot{m})_{in} - (P\widehat{V}\dot{m})_{out}}_{C} \tag{7.5-3}$$

where terms A, B, and C represent, respectively, work associated with the expansion or compression of the system boundaries, shaft work, and flow work.

Substitution of Eq. (7.5-3) into Eq. (7.5-2) and the use of the definition of enthalpy, i.e., $\widehat{H} = \widehat{U} + P\widehat{V}$, give

$$\left[(\widehat{H} + \widehat{E}_K + \widehat{E}_P)\dot{m}\right]_{in} - \left[(\widehat{H} + \widehat{E}_K + \widehat{E}_P)\dot{m}\right]_{out} + \dot{Q}_{int} - P_{sys}\frac{dV_{sys}}{dt} + \dot{W}_s$$
$$= \frac{d}{dt}\left[(\widehat{U} + \widehat{E}_K + \widehat{E}_P)m\right]_{sys} \tag{7.5-4}$$

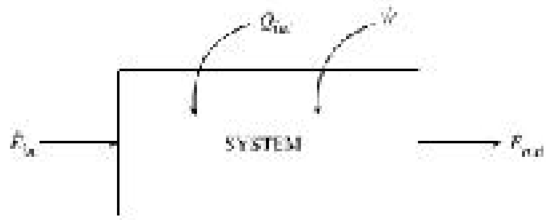


Figure 7.2. Unsteady-state flow system exchanging energy in the form of heat and work with the surroundings.

which is known as the *general energy equation*. Note that under steady conditions Eq. (7.5-4) reduces to Eq. (6.3-9). In terms of molar quantities, Eq. (7.5-4) is written as

$$\left[(\widetilde{H} + \widetilde{E}_K + \widetilde{E}_P)\dot{n}\right]_{in} - \left[(\widetilde{H} + \widetilde{E}_K + \widetilde{E}_P)\dot{n}\right]_{out} + \dot{Q}_{int} - P_{sys}\frac{dV_{sys}}{dt} + \dot{W}_s$$
$$= \frac{d}{dt}\left[(\widetilde{U} + \widetilde{E}_K + \widetilde{E}_P)n\right]_{sys} \tag{7.5-5}$$

When the changes in the kinetic and potential energies between the inlet and outlet of the system as well as within the system are negligible, Eq. (7.5-4) reduces to

$$(\widehat{H}\dot{m})_{in} - (\widehat{H}\dot{m})_{out} + \dot{Q}_{int} - P_{sys}\frac{dV_{sys}}{dt} + \dot{W}_s = \frac{d}{dt}(\widehat{U}m)_{sys} \tag{7.5-6}$$

The accumulation term in Eq. (7.5-6) can be expressed in terms of enthalpy as

$$\frac{d}{dt}(\widehat{U}m)_{sys} = \frac{d}{dt}\left[(\widehat{H} - P\widehat{V})m\right]_{sys} = \frac{d}{dt}(\widehat{H}m)_{sys} - P_{sys}\frac{dV_{sys}}{dt} - V_{sys}\frac{dP_{sys}}{dt} \tag{7.5-7}$$

Substitution of Eq. (7.5-7) into Eq. (7.5-6) gives

$$\boxed{(\widehat{H}\dot{m})_{in} - (\widehat{H}\dot{m})_{out} + \dot{Q}_{int} + V_{sys}\frac{dP_{sys}}{dt} + \dot{W}_s = \frac{d}{dt}(\widehat{H}m)_{sys}} \tag{7.5-8}$$

On a molar basis, Eq. (7.5-8) can be expressed as

$$\boxed{(\widetilde{H}\dot{n})_{in} - (\widetilde{H}\dot{n})_{out} + \dot{Q}_{int} + V_{sys}\frac{dP_{sys}}{dt} + \dot{W}_s = \frac{d}{dt}(\widetilde{H}n)_{sys}} \tag{7.5-9}$$

→ Euler's method:-

→ Euler's method is a numerical method to solve first order first degree differential eqn with a given initial value.

$$\frac{dy}{dt} = f(t,y) \quad , \quad y(t_0) = y_0$$

$$\left.\frac{dy}{dt}\right|_{t=t_0} = f(t_0, y_0)$$

$$y = y_0 + f(t_0, y_0)(t - t_0)$$

$$y_1 = y_0 + f(t_0, y_0)(t_1 - t_0)$$

$$y_2 = y_1 + f(t_0, y_0)(t_2 - t_1)$$

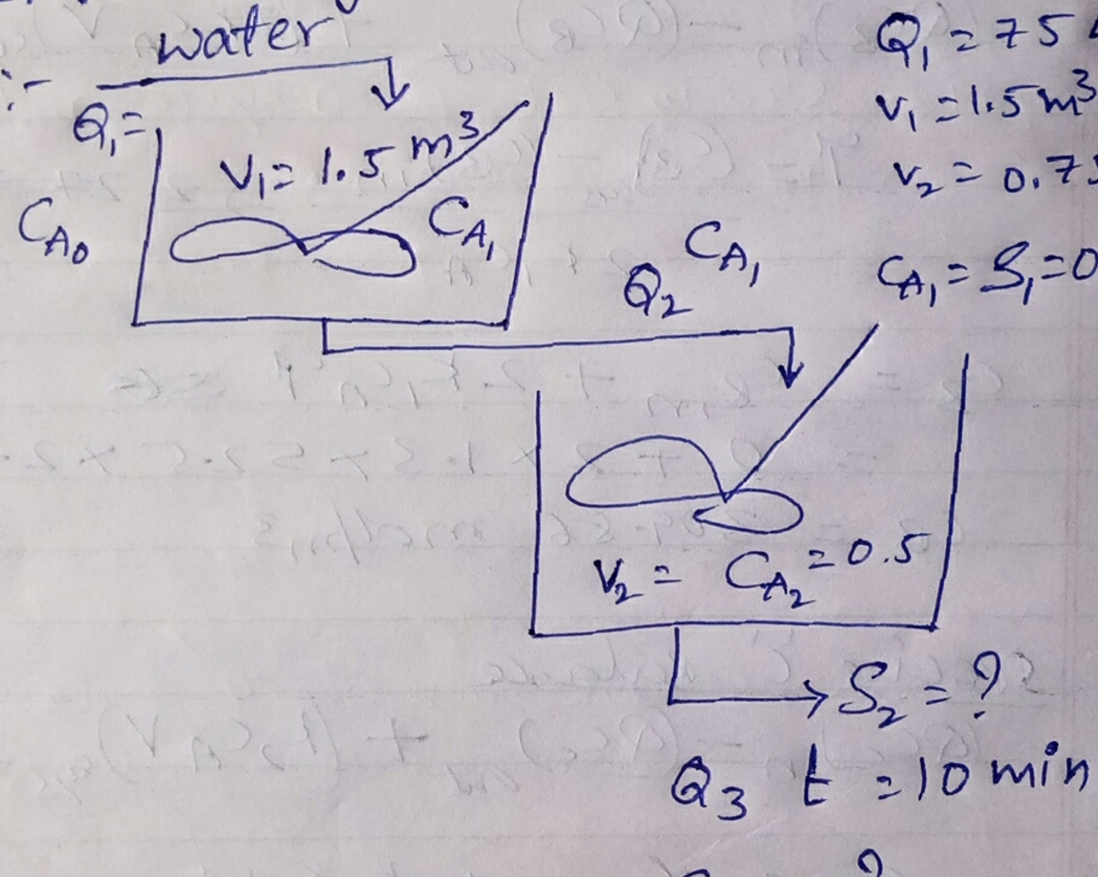
$$y_{n+1} = y_n + f(t_n, y_n) \cdot (t_{n+1} - t_n)$$

$$t_{n+1} - t_n = h \quad , \quad f(t_n, y_n) = f_n$$

$$\boxed{y_{n+1} = y_n + h f_n}$$

(7.2) Two perfectly stirred tanks with capacities of 1.5 and 0.75 m^3 are connected in such a way that the effluent from the first passes into the second. Both tanks are initially filled with salt solution 0.5 kg/L in concentration. If pure water is fed in to the first tank at a rate of 75 L/min, determine the salt concentration in the second tank after 10 minutes?
(Answer: 0.423 kg/L)

Sol :-



$Q_1 = 75$ L/min
$V_1 = 1.5\ m^3 = 1500$ L
$V_2 = 0.75\ m^3 = 750$ L
$C_{A_1} = S_1 = 0.5$ kg/L

$t = 10$ min

$C_{A_2} = ?$

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PAGE No

Assumption

1. Perfectly mixed reactors

$$(C_A)_{sys} = (C_A)_{out} = C_A$$

2. $Q_1 = Q_2 = Q_3 = Q$

Reactor ① balance

$$Q_1 C_{A0} - Q_2 C_{A1} = \frac{dm_1}{dt} = \frac{d(C_{A1} V_1)}{dt} = V_1 \frac{dC_{A1}}{dt}$$

$$\frac{dC_{A1}}{dt} = \frac{Q}{V_1}(C_{A0} - C_{A1})$$

by using Euler's method :-

$$(C_A)_{i+1} = C_{A_i} + \Delta t \left(\frac{Q}{V_1}(C_{A0} - C_{A1})\right)_i$$

Reactor ② balance

$$Q_2 C_{A1} - Q_3 C_{A2} = \frac{dm_2}{dt} = \frac{d(C_{A2} V_2)}{dt} = V_2 \frac{dC_{A2}}{dt}$$

$$\frac{dC_{A2}}{dt} = \frac{Q}{V_2}(C_{A1} - C_{A2})$$

by using Euler's method

$$(C_{A2})_{i+1} = (C_{A2})_i + \Delta t \left(\frac{Q}{V_2}(C_{A1} - C_{A2})\right)_i$$

t	C_{A_1}	C_{A_2}	Q	V_1	V_2	Δt
0	0.5	0.5	75	1500	750	0
2	0.45	0.5	75	1500	750	2
4	0.405	0.49	75	1500	750	2
6	0.365	0.473	75	1500	750	2
8	0.328	0.451	75	1500	750	2
10	0.295	0.427	75	1500	750	2

kg/L = C_{A_2} **Ans**

7.4 a) A stream containing 10% species *A* by weight starts to flow at a rate of 2 kg/min into a tank originally holding 300 kg of pure *B*. Simultaneously, a valve at the bottom of the tank is opened and the tank contents are also withdrawn at a rate of 2 kg/min. Considering perfect mixing within the tank, determine the time required for the exit stream to contain 5% species *A* by weight.

b) Consider the problem in part (a). As a result of the malfunctioning of the exit valve, tank contents are withdrawn at a rate of 2.5 kg/min instead of 2 kg/min. How long does it take for the exit stream to contain 5% species *A* in this case?

(**Answer:** a) 104 min b) 95.5 min)

	Case:1		**Case:2**		
i	Time	x_A	m	$m*x_A$	x_A
0	0	0.00000	300	0	0.00000
1	1	0.00067	299.5	0.2	0.00067
2	2	0.00133	299	0.398330551	0.00133
3	3	0.00199	298.5	0.595000028	0.00199
4	4	0.00264	298	0.790016778	0.00265
5	5	0.00329	297.5	0.983389121	0.00331
6	6	0.00393	297	1.175125346	0.00396
7	7	0.00457	296.5	1.365233719	0.00460
8	8	0.00521	296	1.553722473	0.00525
9	9	0.00584	295.5	1.740599817	0.00589
10	10	0.00647	295	1.925873931	0.00653
11	11	0.00709	294.5	2.109552965	0.00716
12	12	0.00771	294	2.291645045	0.00779
13	13	0.00833	293.5	2.472158268	0.00842
14	14	0.00894	293	2.651100701	0.00905
15	15	0.00955	292.5	2.828480388	0.00967
16	16	0.01015	292	3.004305342	0.01029
17	17	0.01075	291.5	3.17858355	0.01090
18	18	0.01134	291	3.351322971	0.01152
19	19	0.01193	290.5	3.522531536	0.01213
20	20	0.01252	290	3.692217151	0.01273
21	21	0.01310	289.5	3.860387693	0.01333
22	22	0.01368	289	4.027051012	0.01393
23	23	0.01426	288.5	4.19221493	0.01453
24	24	0.01483	288	4.355887245	0.01512
25	25	0.01540	287.5	4.518075723	0.01572
26	26	0.01596	287	4.678788108	0.01630
27	27	0.01652	286.5	4.838032114	0.01689

Case:1

Overall Balance

1. $F_o = F$
2. $d(m)_{sys}/dt = 0$ (since, $(m)_{sys}$=constant)

Component 'A' Balance

$$dx_A/dt = [(F_o x_A)_{in} - (F x_A)_{out}] / (m)_{sys}$$

(By Eulers Method)

$$(x_A)_{i+1} = (x_A)_i + \Delta t \{[(F_o x_A)_{in} - (F x_A)_{out}] / (m)_{sys}\}_i$$

Case:2

Overall Balance

$$F_o - F = d(m)_{sys} / dt$$

(By Eulers Method)

$$(m)_{i+1} = m_i + \Delta t [F_o - F]_i$$

Component 'A' Balance

$$[(F_o x_A)_{in} - (F x_A)_{out}] = [d(m*x_A)_{sys} / dt]$$

(By Eulers Method)

$$(m*x_A)_{i+1} = \{(m*x_A)_i + \Delta t \{[(F_o x_A)_{in} - (F x_A)_{out}]\}_i$$

F_o = Flow rate of entering stream in to the Tank, **kg/min**

28	28	0.01708	286	4.995815429	0.01747
29	29	0.01763	285.5	5.152145714	0.01805
30	30	0.01818	285	5.307030603	0.01862
31	31	0.01873	284.5	5.460477703	0.01919
32	32	0.01927	284	5.612494594	0.01976
33	33	0.01981	283.5	5.763088832	0.02033
34	34	0.02034	283	5.912267943	0.02089
35	35	0.02087	282.5	6.060039428	0.02145
36	36	0.02140	282	6.20641076	0.02201
37	37	0.02192	281.5	6.351389388	0.02256
38	38	0.02244	281	6.494982733	0.02311
39	39	0.02296	280.5	6.637198189	0.02366
40	40	0.02348	280	6.778043125	0.02421
41	41	0.02399	279.5	6.917524883	0.02475
42	42	0.02449	279	7.055650778	0.02529
43	43	0.02500	278.5	7.192428101	0.02583
44	44	0.02550	278	7.327864114	0.02636
45	45	0.02599	277.5	7.461966056	0.02689
46	46	0.02649	277	7.594741136	0.02742
47	47	0.02698	276.5	7.726196541	0.02794
48	48	0.02746	276	7.85633943	0.02846
49	49	0.02795	275.5	7.985176935	0.02898
50	50	0.02843	275	8.112716164	0.02950
51	51	0.02890	274.5	8.238964199	0.03001
52	52	0.02938	274	8.363928095	0.03053
53	53	0.02985	273.5	8.487614883	0.03103
54	54	0.03032	273	8.610031566	0.03154
55	55	0.03078	272.5	8.731185123	0.03204
56	56	0.03124	272	8.851082507	0.03254
57	57	0.03170	271.5	8.969730646	0.03304
58	58	0.03216	271	9.087136441	0.03353
59	59	0.03261	270.5	9.203306769	0.03402
60	60	0.03306	270	9.318248481	0.03451
61	61	0.03350	269.5	9.431968402	0.03500
62	62	0.03395	269	9.544473334	0.03548
63	63	0.03439	268.5	9.65577005	0.03596
64	64	0.03483	268	9.765865301	0.03644
65	65	0.03526	267.5	9.874765811	0.03692
66	66	0.03569	267	9.98247828	0.03739

F = Flow rate of leaving stream from the Tank, **kg/min**
$(m)_{sys}$ = Mass of the System, **kg**
x_A = weight fraction of the component 'A'
t = Time, **minutes**

Answer
Case1: t = 104 minutes at x_A = 0.05
Case2: t = 96 minutes at x_A = 0.05

67	67	0.03612	266.5	10.08900938	0.03786
68	68	0.03655	266	10.19436577	0.03832
69	69	0.03697	265.5	10.29855406	0.03879
70	70	0.03739	265	10.40158086	0.03925
71	71	0.03781	264.5	10.50345274	0.03971
72	72	0.03822	264	10.60417624	0.04017
73	73	0.03863	263.5	10.70375791	0.04062
74	74	0.03904	263	10.80220423	0.04107
75	75	0.03945	262.5	10.89952168	0.04152
76	76	0.03985	262	10.99571671	0.04197
77	77	0.04025	261.5	11.09079575	0.04241
78	78	0.04065	261	11.1847652	0.04285
79	79	0.04105	260.5	11.27763143	0.04329
80	80	0.04144	260	11.3694008	0.04373
81	81	0.04183	259.5	11.46007964	0.04416
82	82	0.04222	259	11.54967425	0.04459
83	83	0.04260	258.5	11.63819091	0.04502
84	84	0.04299	258	11.72563587	0.04545
85	85	0.04337	257.5	11.81201537	0.04587
86	86	0.04374	257	11.89733561	0.04629
87	87	0.04412	256.5	11.98160277	0.04671
88	88	0.04449	256	12.06482302	0.04713
89	89	0.04486	255.5	12.14700248	0.04754
90	90	0.04523	255	12.22814727	0.04795
91	91	0.04559	254.5	12.30826347	0.04836
92	92	0.04596	254	12.38735715	0.04877
93	93	0.04632	253.5	12.46543434	0.04917
94	94	0.04667	253	12.54250107	0.04958
95	95	0.04703	252.5	12.61856331	0.04997
96	**96**	**0.04738**	**252**	**12.69362704**	**0.05037** → **Case2 Answer**
97	97	0.04773	251.5	12.7676982	
98	98	0.04808	251	12.9676982	
99	99	0.04843	250.5	13.1676982	
100	100	0.04877	250	13.3676982	
101	101	0.04911	249.5	13.5676982	
102	102	0.04945	249	13.7676982	
103	103	0.04979	248.5	13.9676982	
104	**104**	**0.05013**	**248**	**14.1676982**	

Case1 Answer (0.05013)

Reference: Ismail Tosun - Modelling in Transport Phenomena-Elsevier Science (2007)