Clarkson University

MASS DIFFUSION

In this section the mass transfer process is described. The Brownian diffusion of small particles and Fick's law are first discussed. This is followed by the presentation of a number of applications.

Brownian Diffusion

Small particles suspended in a fluid undergo random translational motions due to molecular collisions. This phenomenon is referred to as the Brownian motion. The Brownian motion leads to diffusion of particles in accordance with Fick's law. i.e.,

$$J = -D \frac{dc}{dx} \tag{1}$$

where c is the concentration, J is the flux, and D is the diffusion coefficient. When the effect of particle inertia is negligible, using (1) in the equation of conservation of mass for particles leads to

$$\frac{\partial c}{\partial t} + \mathbf{v} \cdot \nabla c = D \nabla^2 c \tag{2}$$

where $\mathbf{v}$ is the fluid velocity vector. The particle mass diffusivity is given by

$$D = \frac{kTC_c}{3\pi\mu d} \tag{3}$$

where C_c is the Cunningham correction given by (3) and k is the Boltzmann constant ($k = 1.38 \times 10^{-16}$ erg/K). The diffusive may be restated as

$$D = \frac{\tau kT}{m} \tag{4}$$

where m is the mass of the spherical particle and τ is its relaxation time.

Table 8 – Particle mass diffusivity.

$d \quad (\mu m)$	$D \quad (cm^2/s)$
10^{-2}	5.24×10^{-4}
10^{-1}	6.82×10^{-6}
1	2.74×10^{-7}
10	2.38×10^{-8}

The mean-square displacement for a Brownian particle is given as

$$\overline{s^2} = 2Dt \qquad \text{(one-dim)} \tag{5}$$

Brownian Motion of Rotation

Aerosol particles may also rotate randomly due to the Brownian effects. The mean-square angle of rotation is given as

$$\overline{\theta^2} = \frac{2kT}{\pi\mu d^3} t \tag{6}$$

Distributions

When the gas is in equilibrium, the aerosol particle will have the same average translational energy as molecules. Thus

$$\frac{1}{2} m\overline{u^2} = \frac{3}{2} kT, \tag{7}$$

and the root-mean-square particle velocity is given by

$$\sqrt{\overline{u^2}} = \sqrt{3kT/m} \tag{8}$$

Under equilibrium, aerosol particles will have a Maxwellian distribution and their concentration in a gravitational field is given by

$$C = C_0 \exp\{-\frac{mg(x - x_0)}{kT}\} \tag{9}$$

Effect of Mass

The diffusivity as given by (3) and (4) is independent of particle density, but heavy particles do not respond swiftly to the molecular impacts. A time dependent analysis leads to

$$s^2 = 2Dt[1 - \tau(1 - e^{-t/\tau})/t] \tag{10}$$

where τ is the particle relaxation time. when $t >> \tau$, (10) reduces to Equation (5).

Aerosols Mean Free Path

The apparent mean free path for aerosol particles λ_α is defined as the average distance that a particle moves before changing its direction by 90°. The average (absolute) velocity of an aerosol particle is $\sqrt{8kT/\pi m}$. From the definition of stop distance it follows that

$$\lambda_\alpha \approx \tau\sqrt{8kT/\pi m} \tag{11}$$

λ_α becomes a minimum for an aerosol particle diameter of about 0.05 μm. λ_α is of the order of 10^{-6} cm for $d \le 5$ μ.

Particle Diffusion to a Wall

For a one-dimensional case, the diffusion equation given by (18) in the absence of a flow field becomes

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial y^2} \tag{12}$$

For an initially uniform concentration of aerosols in the neighborhood of an absorbing wall, the initial and boundary conditions are: $C(y,0) = C_0$ and $C(0,t) = 0$. The solution to Equation (28) then becomes

$$C(y,t) = C_0 \mathrm{erf}(y/\sqrt{4Dt}), \tag{13}$$

where

$$\mathrm{erf}(\xi) = \frac{2}{\sqrt{\pi}}\int_0^\xi e^{-\xi^2} d\xi, \qquad \mathrm{erf}(0) = 0,\ \mathrm{erf}(\infty) = 1 \tag{14}$$

The variation of concentration profile with time are shown in Figure 1. (Note that y has the same unit as $\sqrt{Dt}$.)

The flux to the wall then is given by

$$J = -D\left.\frac{\partial c}{\partial x}\right|_{y=0} = C_0\sqrt{\frac{D}{\pi t}} \tag{15}$$

where C_0 is the particles number concentration at the initial time.

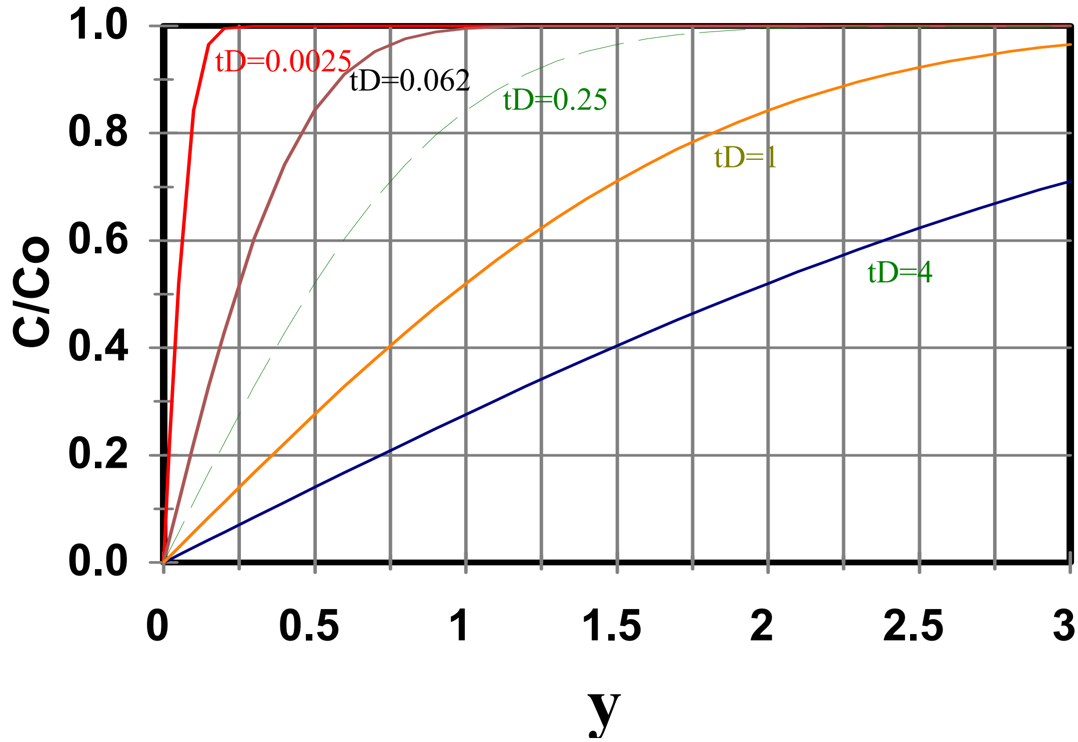

Figure 1. Variation of concentration profile with time.

The corresponding deposition velocity, which is defined as flux per unit concentration, then is given by

$$u_D = \frac{J}{C_0} = \sqrt{\frac{D}{\pi t}} = \frac{D}{\delta_c} \tag{16}$$

Here δ_c is the diffusion boundary layer thickness given as

$$\delta_c = \sqrt{\pi D t} \tag{17}$$

The corresponding diffusion force is defined as

$$F_d = 3\pi\mu d u_D / C_c \tag{18}$$

The total number of particles that is deposited in an interval dt is given as

$$dN = Jdt = C_0\sqrt{\frac{D}{\pi t}}dt \tag{19}$$

The total number of particles that are deposited per unit area in the time interval 0 to t may be obtained by integrating Equation (19). Thus,

$$N = C_0\sqrt{\frac{4Dt}{\pi}}\,. \tag{20}$$

Tube Deposition

Consider a constant velocity gas flow in a tube of length L and radius R. The residence time is $t = L/u$ where u is the gas velocity. Assuming that the wall deposition process is similar to that of a uniform concentration near a wall, and using (20) it follows that

$$C_{out} - C_{in} = -N\frac{2R\pi L}{\pi R^2 L}, \qquad N = C_{in}\sqrt{\frac{4DL}{\pi u}}\,, \tag{21}$$

or

$$\frac{C_{out}}{C_{in}} = 1 - \frac{4}{\sqrt{\pi}}\sqrt{\frac{DL}{uR^2}}\,. \tag{22}$$

A detailed duct flow analysis shows

$$\frac{C_{out}}{C_{in}} = 1 - 2.56\phi^{2/3} + 1.2\phi + 0.177\phi^{4/3},\ \phi = \frac{DL}{uR^2}\,. \tag{23}$$

Diffusion Velocity

The diffusion velocity is defined as

$$U_D = \frac{J}{C_0}\,. \tag{24}$$

Similarly, a diffusion force may be defined as

$$F_{diff} = 3\pi\mu u_d / C_c \tag{25}$$

Convective Diffusion to a Flat Plane

Consider a laminar boundary layer flow over a flat plane as shown. The equations of motion and mass diffusion are

$$u\frac{\partial u}{\partial x}+v\frac{\partial u}{\partial y}=\nu\frac{\partial^2 u}{dy^2} \tag{26}$$

$$\frac{\partial u}{\partial x}+\frac{\partial v}{\partial y}=0 \tag{27}$$

$$u\frac{\partial c}{\partial x}+v\frac{\partial c}{\partial y}=D\frac{\partial^2 c}{\partial y^2} \tag{28}$$

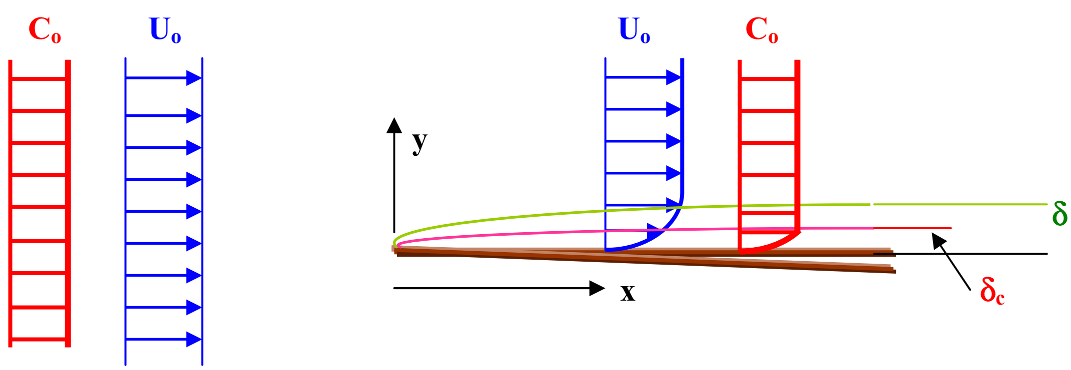

Figure 2. Schematics of boundary layer flow over a flat plate.

The boundary conditions are

$$\text{At } y=0, \qquad u=v=c=0 \tag{29}$$

$$\text{As } y\to\infty, \qquad u=U_0, c=c_0 \tag{30}$$

Introducing similarity variable,

$$\eta=y\sqrt{\frac{U_0}{\nu x}},\ \psi=\sqrt{\nu U_o x}f(\eta),\ \frac{u}{U_0}=f'(\eta),\ c=c(\eta), \tag{31}$$

Equations (26) – (28) reduce to

$$ff''+2f'''=0, \qquad f(0)=f'(0)=0, f'(\infty)=1 \tag{32}$$

$$c''+\frac{1}{2}S_c fc'=0, \qquad c(0)=0,\ c(\infty)=c_0 \tag{33}$$

where the Schmidt number is defined as

$$S_c=\frac{\nu}{D}. \tag{34}$$

For a large Schmidt number, $\delta_c << \delta$ as shown in the figure.

The solution to the Blasius equation (32) is well know and leads to

$$\delta=5\sqrt{\frac{\nu x}{U_0}},\ f''(0)=\gamma=0.332. \tag{35}$$

Near the plate then

$$f \simeq \frac{\gamma}{2}\eta^2+\dots \tag{36}$$

Using (36) in Equation (33), after integration we find

$$C=\frac{C_0\int_0^\eta \exp(-\gamma_1 s_c z^3)dz}{\int_0^\infty \exp(-\gamma_1 s_c z^3)dz},\ \gamma_1=\frac{\gamma}{12} \tag{37}$$

Noting that

$$\int_0^\infty [\exp(-\gamma_1 s_c z^3)]dz=\frac{1}{\sqrt[3]{\gamma_1 s_c}}\int_0^\infty [\exp(-z_1^3)]dz_1=\frac{\Gamma(1/3)}{3\sqrt[3]{\gamma_1 s_c}}, \tag{38}$$

We find

$$\frac{c}{c_0}=\frac{\sqrt[3]{\gamma_1 s_c}}{0.89}\int_0^\eta [\exp(-\gamma_1 s_c z^3)]dz \tag{39}$$

Variation of concentration profile as given by Equation (39) is shown in figure 3. The mass flux is then given by

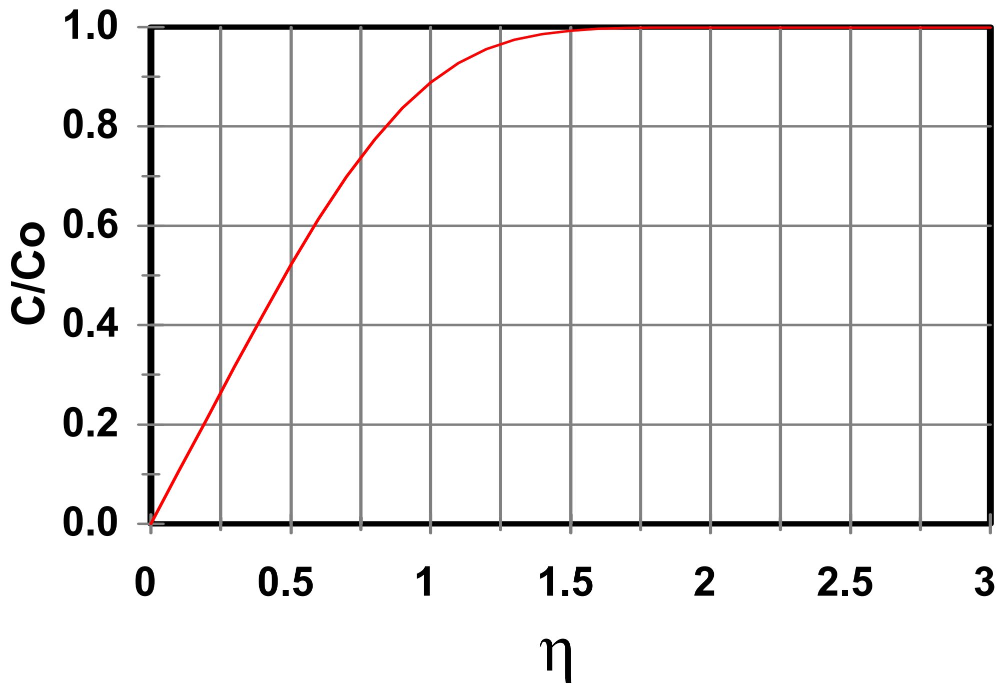

Figure 3. Variation of concentration profile with η for $\gamma_1 Sc = 1$.

$$J = D\left[\frac{\partial c}{\partial y}\right]_{y=0} = Dc_0 \frac{\sqrt[3]{(\gamma_1 s_c)}}{0.89}\sqrt{\frac{U_0}{\nu x}} = 0.34 Dc_0 \sqrt[3]{s_c}\sqrt{\frac{U_0}{\nu x}}. \tag{40}$$

The diffusion boundary layer thickness is then given by

$$\delta_c = \frac{Dc_0}{J} \approx \frac{3}{\sqrt[3]{s_c}}\sqrt{\frac{\nu x}{U_0}} \approx \frac{0.6\delta}{\sqrt[3]{s_c}} \tag{41}$$

The total diffusion

$$I = \int_0^L J dx = 0.68 Dc_0 \sqrt[3]{s_c}\sqrt{R_{eL}}, \qquad R_{eL} = \frac{U_o L}{\nu} \tag{42}$$

Diffusion in a Tube Flow

Consider a laminar flow in a tube with $u = u_0 (1 - \frac{r^2}{R^2})$. Let $y = R - r$. At distances very close to the wall, that is for small y,

$$u \simeq u_0 \frac{2y}{R} + \ldots \tag{43}$$

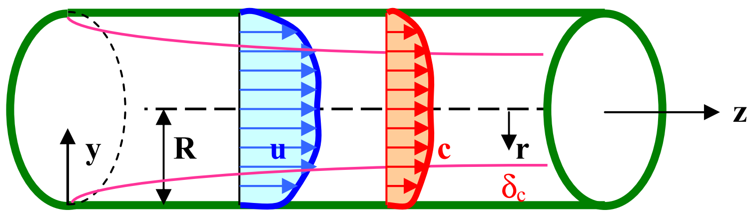

Figure 4. Schematics of convective diffusion in a pipe.

The convective diffusion equation then becomes

$$\frac{2v_0}{R} y \frac{\partial c}{\partial x} = D \frac{\partial^2 c}{\partial y^2} \tag{44}$$

The appropriate boundary conditions are

$$c = 0 \text{ at } y = 0, \; c = c_0 \text{ at } y \to \infty \tag{45}$$

Introducing similarity variable

$$\eta = \sqrt[3]{\frac{u_0}{DR}} \frac{y}{\sqrt[3]{x}} \tag{46}$$

Equation (44) may be restated as

$$c'' + \frac{2}{3} \eta^2 c' = 0 \tag{47}$$

The solution to (47), which satisfies (45), is given by

$$c = \frac{c_0 \int_0^{\eta} \exp\{\frac{-2}{9} \eta_1^3\} d\eta_1}{\int_0^{\infty} \exp\{\frac{-2}{9} \eta_1^3\} d\eta_1} \tag{48}$$

The diffusion to the wall is given as

$$J = D\left[\frac{\partial c}{\partial y}\right]_{y=0} = \frac{\dfrac{Dc_0}{\sqrt[3]{x}}\sqrt[3]{\dfrac{u_0}{DR}}}{\int_0^{\infty}\exp(-\frac{2}{9}\eta_1^3)d\eta_1} \tag{49}$$

$$J = 0.67 c_0 D\sqrt[3]{\frac{u_0}{DRx}} \tag{50}$$

The diffusion layer thickness is determined by

$$\delta_c = \frac{Dc_0}{J} = \frac{\sqrt[3]{R^2 x}}{0.67 s_c^{1/3} R_{eR}^{1/3}} = \frac{1}{0.67}\sqrt[3]{\frac{R^2 x}{s_c R_{eR}}} \tag{51}$$

where

$$R_{e_R} = \frac{u_0 R}{\nu} \tag{52}$$

The total diffusion for a length L is given by

$$I = 2\pi R\int_0^L J dx = 2.01\pi c_0 DR\sqrt[3]{\frac{u_0 L^2}{DR}} \tag{53}$$

Diffusion in a Stream in a Tube

The equation governing the convective diffusion in a tube is given as

$$\frac{\partial c}{\partial t} + u(r)\frac{\partial c}{\partial x} = D(\frac{\partial^2 c}{\partial r^2} + \frac{1}{r}\frac{\partial c}{\partial r} + \frac{\partial^2 c}{\partial x^2}) \tag{54}$$

with

$$u(r) = 2U(1 - \frac{r^2}{R^2}) \tag{55}$$

where U is the mean velocity in the tube. In a coordinate system moving with the mean fluid velocity U, Equation (54) may be restated as

$$\frac{\partial c}{\partial t} + V(1 - \frac{2r^2}{R^2})\frac{\partial c}{\partial x} = D(\frac{\partial^2 c}{\partial r^2} + \frac{1}{r}\frac{\partial c}{\partial r}), \tag{56}$$

where the axial diffusion $\frac{\partial^2 c}{\partial x^2}$ is neglected.

For zero flux to the wall, the boundary condition at the tube surface is given as

$$\left[\frac{\partial c}{\partial r}\right]_R = 0 \tag{57}$$

As a first approximation, $\frac{\partial c}{\partial t}$ in the moving frame is negligibly small and

$$\frac{\partial c}{\partial x} = \text{const} = \frac{\partial \bar{c}}{\partial x} \tag{58}$$

Now solving Equation (56) for c, it follows that

$$c = c_o + \frac{UR^2}{4D}\frac{\partial \bar{c}}{\partial x}\left(\frac{r^2}{R^2} - \frac{1}{2}\frac{r^4}{R^4}\right), \qquad \frac{\partial c}{\partial t} = 0 \tag{59}$$

where

$$c_o = [c]_{r=0}, \text{ and } \quad \bar{c} = \frac{1}{A}\int_A c\,dA = \frac{1}{\pi R^2}\int_0^R 2\pi r c\,dr = \frac{2}{R^2}\int_0^R c r\,dr \tag{60}$$

Using (59) in (60), the value of c_o may be evaluated and then

$$c = \bar{c} + \frac{R^2 U}{4D}\frac{\partial \bar{c}}{\partial x}\left(-\frac{1}{3} + \frac{r^2}{R^2} - \frac{1}{2}\frac{r^4}{R^4}\right), \quad \frac{\partial c}{\partial t} = 0 \tag{61}$$

The total flow of substance across the pipe then is given by

$$Q_c = 2\pi\int_0^R c(u - U) r\,dr = -(\pi R^2)\frac{R^2 U^2}{48D}\frac{\partial \bar{c}}{\partial x}. \tag{62}$$

The flux

$$J = \frac{Q}{\pi R^2} = -\left(\frac{R^2 U^2}{48D}\right)\frac{\partial \bar{c}}{\partial x} \tag{63}$$

has the same form as Fick's law with an effective diffusivity

$$D_{eff} = \frac{R^2 U^2}{48D}. \tag{64}$$

In the next approximation we drop the assumption that $\frac{\partial \bar{c}}{\partial x} = \text{const.}$, thus

$$\frac{\partial \bar{c}}{\partial t} = -\frac{\partial}{\partial x} J = D_{eff} \frac{\partial^2 \bar{c}}{\partial x^2} \tag{65}$$

Equation (65) is applicable if the Peclet number, $P_e = \frac{2UR}{D} = R_e S_c$ satisfy

$$\frac{L}{R} >> P_e >> 14 \tag{66}$$

If a certain amount N of substance is introduced at $x = 0$, $t = 0$, that is

$$c = \frac{N}{\pi R^2} \delta(x) \qquad \text{at } t = 0, \tag{67}$$

Then the solution to Equation (65) is given as

$$\bar{c} = \frac{1}{2} \frac{N}{\pi R^2} \frac{1}{\sqrt{\pi D_{eff} t}} \exp\{-\frac{(x - Ut)^2}{4 D_{eff} t}\}. \tag{68}$$

Variation of concentration as a function of space and time are shown in Figure 5. It is seen that the concentration travels like a wave but also dispersed along it path.

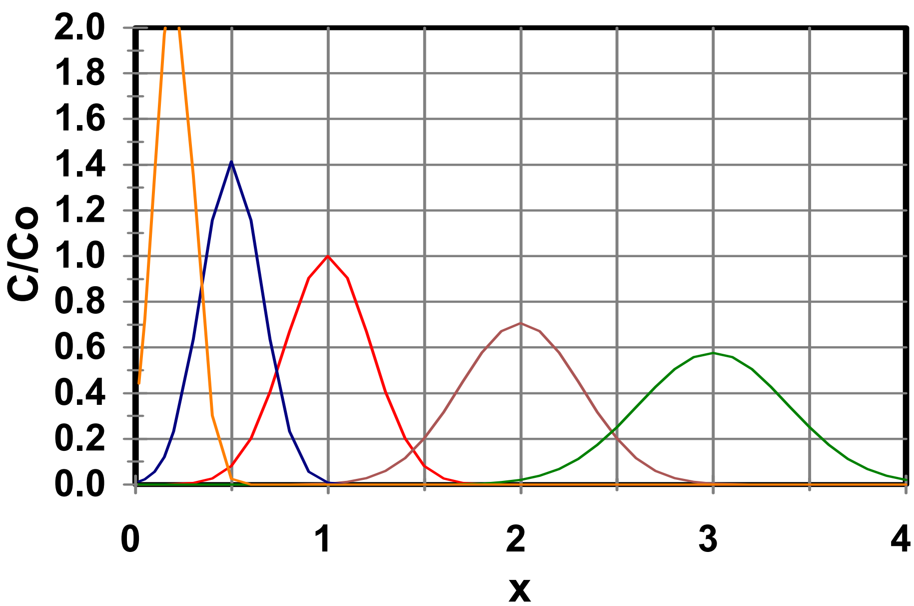

Figure 5. Variations of concentration along the tube at different times.