

# Simulation of the Single Uphill and Osmotic Diffusion

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Received 12 October 2016

Revised 19 November 2016; Accepted 25 December 2016

**Abstract:** Uphill diffusion is a process of mass transmission in which the diffusion flux goes up to high concentration region and the mass flux of osmotic diffusion is not vanishing, when concentration gradient is equal to zero. Most of the uphill and osmotic diffusion takes place in multicomponent systems and the cause of uphill diffusion is the diffusion flux of any species is coupled with that of its partner species. In this paper, the uphill and osmotic diffusion in single component systems (single uphill and osmotic diffusion) are presented and simulated. Results showed that: i) The uphill and osmotic diffusion can take place for single component systems; ii) the cause of single uphill and osmotic diffusion is thermal velocity of molecules in low concentration region is greater than that in high concentration region; iii) simulated results agree with the theory.

*Keywords:* Single uphill and osmotic for single component systems.

## 1. Introduction

Based on direction and value of diffusion flux, diffusion can be divided into four types (Fig.1) [1]:  
i) Downhill diffusion (normal diffusion): the diffusion flux goes from a high concentration area to a low concentration area; ii) Uphill diffusion: the diffusion flux goes up to higher concentration area; iii) Diffusion barrier: concentration gradient is not equal to zero, but diffusion flux is vanishing; iv) Osmotic diffusion: although concentration gradient is equal to zero, diffusion flux is not vanishing.

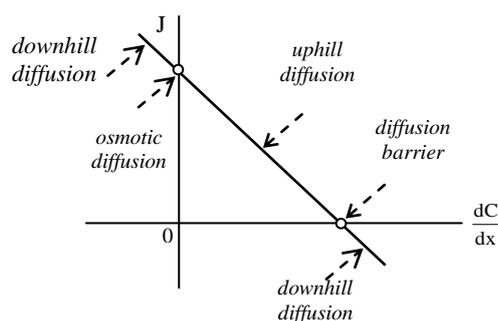


Figure 1. The diffusion classification.

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Uphill and osmotic diffusion is an interesting phenomenon of the diffusion, which is studied since 1949 by L. Darken [2]. Up to now, uphill and osmotic is still being studied and applied [3-13]. Most of the uphill and osmotic diffusion occur for quadratic and ternary systems (two and three components) and cause of the uphill and osmotic diffusion is the diffusion flux of any species is coupled with that of its partner species [1, 5, 11, 13]. However, the uphill and osmotic diffusion can take place in single components (there is only species that diffuses) [14, 15].

## 2. Single uphill diffusion

Assume that the diffusion process take place in the two region 1 and 2. Based on kinetic theory of gasses, in the general case, the thermal velocity ( $u_1$ ) of particles in low concentration region 1 is different to the thermal velocity ( $u_2$ ) in high concentration region 2, the mass flux  $J_1$  goes from region 1 to region 2 and  $J_2$  goes from region 2 to region 1 are determined by:

Table 1. The classification of diffusion by the kinetic theory of gasses.

	$u_1$ and $u_2$	diffusion flux	Diffusion type
$\Delta C = C_2 - C_1 > 0$ ( $C_2 = \alpha C_1$ )	$u_1 = u_2$	$J < 0$	Fick's
	$u_1 < \alpha u_2$	$J < 0$	downhill
	$u_1 = \alpha u_2$	$J = 0$	barrier
	$u_1 > \alpha u_2$	$J > 0$	uphill

$$J_1 = C_1 u_1 \tag{1a}$$

$$J_2 = C_2 u_2 \tag{1b}$$

where  $C_1$  and  $C_2$  are concentration in region 1 and 2. The total of mass flux is:

$$J = J_1 - J_2 = (u_1 C_2 - u_2 C_2) \tag{2}$$

The equation (2) is the formula of general diffusion flux. Direction of diffusion flux is dependent on the difference of concentration and thermal velocity in two regions ( $u_1, C_1$  and  $u_2, C_2$ ). When the concentration gradient is greater than zero with  $C_2 = \alpha C_1$  ( $\alpha > 1$ ), based on equation (2) the diffusion process can be classified to four types: i) if the thermal velocity  $u_1$  in low concentration region is not equal to  $\alpha$  times that  $u_2$  in high concentration region, the diffusivity is positive and mass flux goes to the lower concentration region ( $J < 0$ ), that is downhill diffusion; ii) when  $u_1$  is  $\alpha$  times more than  $u_2$  the diffusivity is negative and diffusion flux goes to the higher concentration region ( $J > 0$ ), that is uphill diffusion; iii) if  $u_1$  is  $\alpha$  times larger than  $u_2$ , diffusion flux vanishes ( $J = 0$ ), that is diffusion barrier; iv) when  $u_1$  equals  $u_2$ , the downhill diffusion becomes Fick's diffusion.

However, according to Lars Onsager the driving force in diffusion is the gradient of chemical potential ( $\mu$ ). Based on the irreversible thermodynamic theory, diffusion flux  $J$  is directly proportional to the gradient of chemical potential  $\mu$  and can be written by following form [16]:

$$J = -L \frac{\partial \mu}{\partial x} \tag{3}$$

in which  $L$  is phenomenological coefficient. Chemical potential is determined by:

$$\mu = \mu_0 + kT \ln C \tag{4}$$

$\mu_0$  is the standard chemical potential. We have:

$$J = -L \frac{\partial \mu}{\partial C} \frac{\partial C}{\partial x} = -D \frac{\partial C}{\partial x} \tag{5}$$

where diffusivity D is:

$$D = L \frac{\partial \mu}{\partial C} \tag{6}$$

For macroscopic description the approximation can be used:

$$\frac{\partial \mu}{\partial C} \approx \frac{\mu_2 - \mu_1}{C_2 - C_1} \tag{7}$$

Chemical potentials  $\mu_1$  and  $\mu_2$  are:

$$\mu_1 = \mu_0 + kT_1 \ln C_1 \tag{8a}$$

$$\mu_2 = \mu_0 + kT_2 \ln C_2 \tag{8b}$$

Suppose that the diffused particles are similar to the ideal gas molecules, so the temperature (T) is directly proportional to the square of thermal velocity (u):

$$T = \frac{m_\mu}{3k} u^2 \tag{9}$$

where  $m_\mu$  is molar mass and k is Boltzmann’s constant. Combining (9) with (8a), we have:

$$D = L \frac{m_\mu}{3} \frac{(u_2^2 \ln C_2 - u_1^2 \ln C_1)}{C_2 - C_1} \tag{10}$$

Based on equation (5) and (10), when the concentration gradient is greater than zero with  $\ln C_2 = \beta^2 \ln C_1$  ( $\beta > 1$ ), the diffusion can be classified also to four types (Tab. 2)

Table 2. The classification of diffusion by the thermodynamic theory.

	<b><math>u_1</math> and <math>u_2</math></b>	<b>diffusion flux</b>	<b>Diffusion type</b>
<b><math>\Delta C = C_2 - C_1 &gt; 0</math></b> ( $\ln C_2 = \beta^2 \ln C_1$ )	$u_1 < \beta u_2$	$J < 0$	Fick’s
	$u_1 < \beta u_2$	$J < 0$	downhill
	$u_1 = \beta u_2$	$J = 0$	barrier
	$u_1 > \beta u_2$	$J > 0$	uphill

Both the kinetic theory of gasses and thermodynamic show when thermal velocity of molecules in the low concentration region is greater than that in the high concentration region, the uphill diffusion can occurs.

### 3. Random walks theory and diffusion

A random particle in a one dimension [17, 18], which begins at  $x = 0$  and the length of all steps are  $l$  (Fig. 2).

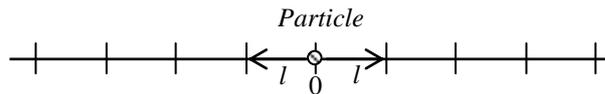


Figure 2. Random walk modeling in one dimension

After each time interval  $\tau$  the particle has an equal probability of moving left or right. The direction of each step is independent of the previous one. We can denote the displacement at each step by  $s_i$ : i)  $s_i = +1$  with 0.5 probability; ii)  $s_i = -1$  with 0.5 probability. Then after  $N$  steps in the random walk, the displacement  $x$  of the atom is:

$$x(N) = \sum_{i=1}^N s_i \tag{11}$$

and the displacement squared is:

$$x^2(N) = \left( \sum_{i=1}^N s_i \right)^2 \tag{12}$$

The average distance the particle has moved, which is immediately obvious that with the equal probabilities to go left and right:

$$\langle x(N) \rangle = 0 \tag{13}$$

that is, the average position will always be at the origin. But this does of course not mean that the particle always is at zero. It means that the probability of finding the particle somewhere is centered at  $x = 0$ , but naturally the probability distribution gets wider with increasing numbers of steps  $N$ . To get a handle on the broadening, let us consider the squared displacement, Eq. 13. We can rewrite this as:

$$x^2(N) = \left( \sum_{i=1}^N s_i \right)^2 = \sum_{i=1}^N s_i \sum_{j=1}^N s_j = \sum_{i=1}^N s_i^2 + \sum_{j=1}^N \sum_{\substack{j=1 \\ j \neq i}}^N s_i s_j \tag{14}$$

Then consider the pair  $s_i s_j$  for a given pair  $i, j$  ( $j \neq i$ ). This quantity will be:

- i)  $s_i = +1$  with 0.5 probability;
- ii)  $s_i = -1$  with 0.5 probability.

So on average the sum over  $s_i s_j$  will be zero. But on the other hand:

$$s_i^2 = 1 \tag{15}$$

independently of whether  $s_i$  is  $+1$  or  $-1$ . Hence the average after  $N$  steps will be:

$$\langle x^2(N) \rangle = N \tag{16}$$

From the atomistic point of view, diffusion is considered as a result of the random walk of the diffusing particles [17, 18].

#### 4. Program and results of the simulation

Simulations of the uphill and osmotic diffusion were executed in the two dimensions. Diffusion process is done on the two regions 1 and 2 of diffused space. The number of particle  $N_1$  and  $N_2$  are chosen deliberately and the positions of particles are chosen randomly in region 1 and 2. A particle can jump to one of the allowed directions by a displacement  $x_i = x_i + \Delta x$  and  $y_i = y_i + \Delta y$ . The walk probabilities of every particle from a position to a nearest position are the same and equal to 0.25 in

both parts. The velocities of a random walk are differently in part 1 and part 2 ( $u_1$  and  $u_2$ ) and which can be changed. We choose that the time of a random walk in the regions 1 and 2 are the same and equal to 1 ms ( $\tau_1 = \tau_2 = \tau = 1\text{ms}$ ), so the length of the random walk step in part 1 and 2 are:  $\Delta x_1 = \Delta y_1 = u_1\tau$  and  $\Delta x_2 = \Delta y_2 = u_2\tau$ .

The program of simulation is written by the Processing language. Simulated results are presented by the motion pictures on the monitor of the computer. Fig.3a shows the positions of particles in regions 1 and 2 at the initial time  $t = 0$ , the number of particle in two parts are the same and equal to 100 ( $N_1 = N_2 = 100$ ). Fig.3b presents the pictures of the positions of particles after the 10 minutes of diffusion, the number of particle in regions 1 and 2 are 74 and 126 ( $N_1 = 74$  and  $N_2 = 126$ ). Fig.3c shows the number of particles after the 20 minutes of diffusion are 67 and 143 ( $N_1 = 67$  and  $N_2 = 143$ ). Results show:

i) At the initial time ( $t = 0$ ): although gradient of concentration is equal to zero, the diffusion process occurs with a diffusion flux goes from region 1 (where the velocity of particles are higher) to region 2 (where the velocity of particles are lower). That is the osmotic diffusion process;

ii) After initial time ( $t = 0$ ): the concentration in part 2 is greater than that in part 1, but there is a diffused flux that goes from region 1 (low concentration region) to region 2 (high concentration region). That is the uphill diffusion.

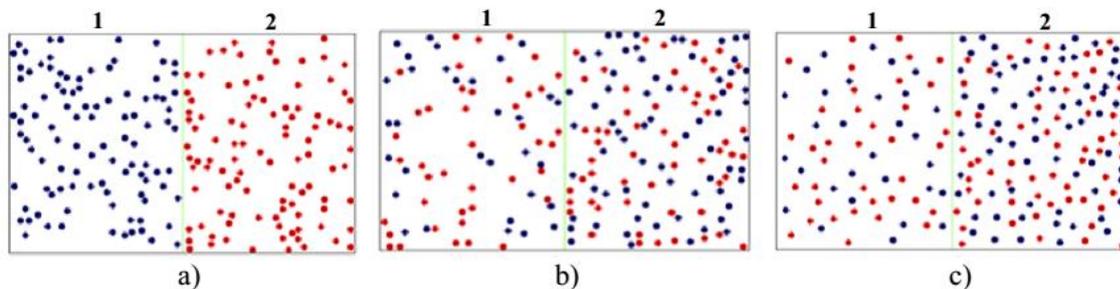


Figure 3. Result of the simulation at the simulated time of  $t$ :  
a)  $t = 0$ , b)  $t = 10$  minutes and c)  $t = 20$  minutes

## 5. Conclusion

Simulated results have shown in single component systems, when thermal velocity in low concentration region is greater than that in high concentration region, uphill and osmotic diffusion can take place. Results of the simulation agree with theory, both have shown that: although the uphill and osmotic diffusion for single component is contrary to Fick's laws, which can occur.

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