

Module 8: "Stability of Colloids"

Lecture 39: ""

The Lecture Contains:

Kinetics of Coagulation

- Rapid Coagulation

 **Previous** **Next** 

Module 8: "Stability of Colloids"

Lecture 39: ""

Kinetics of Coagulation

Equilibrium thermodynamics does not dictate the rate at which processes occur. Many colloidal dispersions have kinetic stability, even though they are unstable thermodynamically. Therefore, the kinetics of coagulation is equally important for the study of stability of colloids.

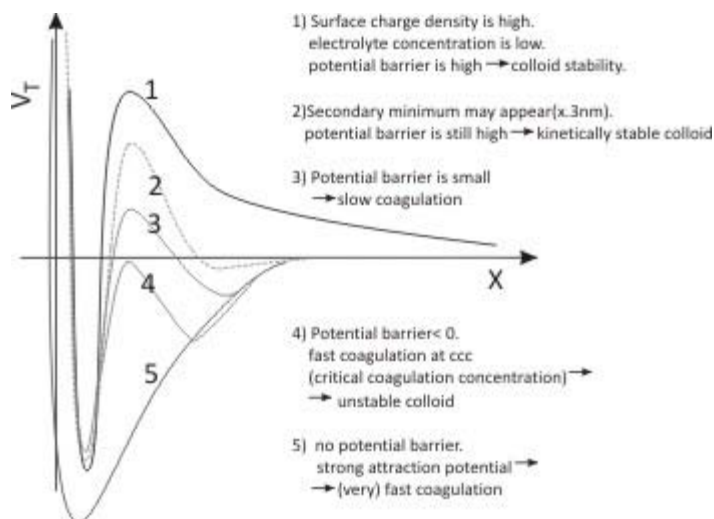


Fig. 10.7: Conditions of colloid stability

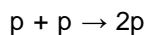
Energy between two colloidal particles can be represented by the above figure. When there is some energy barrier, ($\sim kT$) the coagulation is called slow coagulation (case 3 in Fig. 10.7). In the absence of an energy barrier, the coagulation is rapid, limited only by the rate of diffusion towards each. Coagulation will occur between two particles when they are at the separation of global minimum of interaction energy. This is the condition when the coagulation is thermodynamically favorable. In this section we will discuss the study the kinetics of coagulation for both slow coagulation and rapid coagulation.

Module 8: "Stability of Colloids"

Lecture 39: ""

Rapid Coagulation

Rapid coagulation was studied by Smaluchowski and Einstein in 1917. The simplest case for rapid coagulation would be when interaction energy between two particles is zero in the entire region till the contact distance, where it goes to minus infinity (Fig. 10.8). So, there is perfect sink at the point of contact which means that once the particles are in contact, they will always stick together i.e. particles undergoing random Brownian movement collide and stay in contact. We can say that there is a pseudo chemical reaction represented as



which is an irreversible reaction. In other words we can say that 2 free particles combined to form a doublet (ignoring higher order clusters, as they are rare initially). For simplification we can assume the particles are spheres of radius 'R'. It is assumed that diffusivity is not affected by near by molecule thus hindered diffusion is ignored.

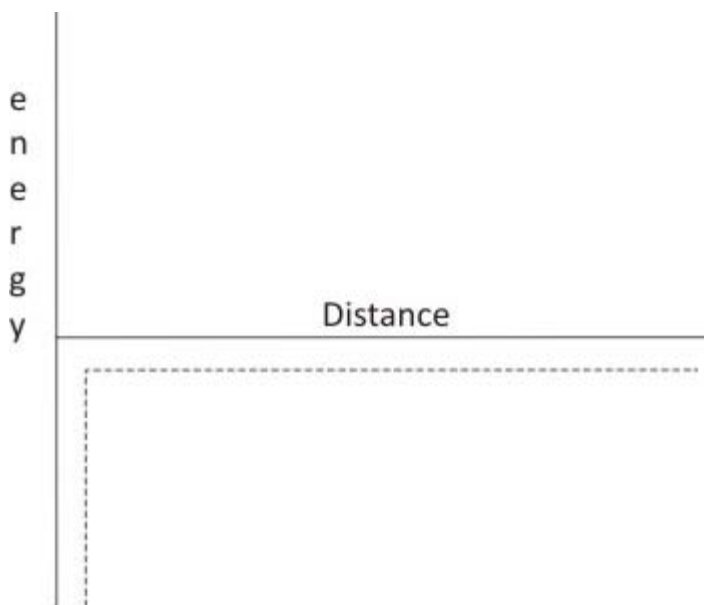


Fig. 10.8: Energy for rapid coagulation (Assumed)

Module 8: "Stability of Colloids"

Lecture 39: ""

Let us take a reference particle which is assumed to be stationary and all other particles are approaching towards it. Consider a spherical shell surrounding the reference particle as shown in the figure below.

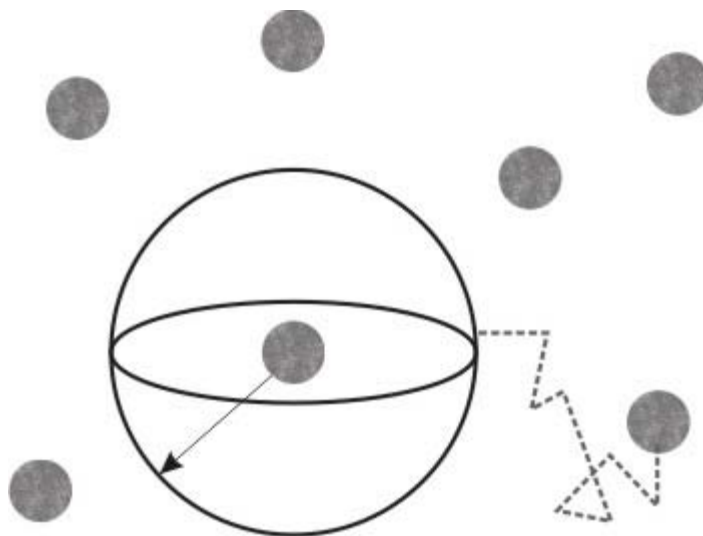


Fig. 10.9: Theoretical spherical surface surrounding a reference particle

Number of particle crossing the spherical shell per unit area per unit time can be written by taking into account the diffusion of particles due to concentration gradient given by Fick's law and energy of attraction between the particles. Thus flux ' j ' is given by

$$jA = -4\pi r^2 \left(D \frac{dN}{dr} + \frac{N}{f} \frac{d\phi}{dr} \right) \quad (10.17)$$

where r is the center to center distance between the two particles, N is number of particles per unit volume and f is friction factor. Second term in right hand side of eq. (10.17) would be zero for r greater than $2R$ because we have assumed that energy of interaction between two particles is zero.

$$\phi = 0 \text{ for all } r > 2R$$

$$\phi = -\infty \text{ for all } r = 2R$$

Module 8: "Stability of Colloids"

Lecture 39: ""

In this case only concentration gradient is driving the coagulation. At steady state number of particles crossing the surface would be constant so left hand side of eq.(10.17) is constant. Thus,

$$\frac{d(jA)}{dr} = 0$$

Applying this condition in equation (10.17) would give a second order differential equation for steady state diffusion. Assuming concentration of particle as $r \rightarrow \infty$ is N_∞ and $N=0$ at $r=2R$. With these boundary conditions we can integrate equation (10.17) as

$$\int_{\infty}^{2R} jA \frac{dr}{4\pi r^2} = -D \int_{N_\infty}^0 dN$$

On integration and substitution of limits we get,

$$jA = -8RD N_\infty \quad (10.18)$$

We have assumed that reference particle is stationary. In general all particles would be approaching towards each other. We can allow for the fact that all particles are in motion by using the sum of the diffusion constants of the two colliding particles. So if we want remove the restriction that the reference is stationary, then we have to replace diffusion coefficient 'D' by '2D' when the particles are of same size or $(D_1 + D_2)$, in general). This would take account of relative diffusion of all particles in each other. Thus number of particles crossing the spherical shell per unit time at steady state is

$$jA = -16RD N_\infty$$

Module 8: "Stability of Colloids"

Lecture 39: ""

As all the particles crossing the shell are coagulating and each collision results in coagulation, the coagulation rate is simply the collision rate. Thus it can be said that jA is the rate of coagulation per particles per unit time. If we consider all the particles, the rate at which particles are coagulating is given by

$$rate = R_f = \frac{dN}{dt} = -16\pi RD N^2 = -K_r N^2 \quad (10.19)$$

which has the characteristic form of a second-order process with a diffusion-controlled rate.

In the above equation, K_r is the rate constant for rapid coagulation given by

$$K_r = 16\pi RD \quad (10.20)$$

Similar to molecular kinetics, we can express the rate coefficient in the form of an Arrhenius expression:

$$k = A' \exp(-E_a/RT)$$

In our case the pre-exponential factor is simply the collision frequency. We have assumed that when particles collide they stick. There is no barrier in place and thus the activation energy is zero. Hence K_r , in this case is independent of temperature.

From Einstein-Stokes equation for the Brownian self-diffusion, diffusion coefficient for spherical particles is given by

$$D = \frac{kT}{f} = \frac{kT}{6\pi R\mu} \quad (10.21)$$

Combining equation (10.19) and (10.20) we get

$$D = \frac{8kT}{3\mu}$$

Module 8: "Stability of Colloids"

Lecture 39: ""

Thus diffusion coefficient is independent of particle size. Solving this differential equation (10.18) we can get concentration as a function of time. Initial concentration can be taken as N_0 . Applying this as initial condition and solving it we get

$$t = \frac{1}{16\pi RD} \left(\frac{1}{N} - \frac{1}{N_0} \right) \quad (10.22)$$

From this equation we can get half life for coagulation as

$$t_{1/2} = \frac{3\mu}{8kTN_0} \quad (10.23)$$

Experiments are done in volume fraction so it would be better to write $t_{1/2}$ in terms of volume fraction.

$$\text{Volume fraction of particle} = \phi_v = \frac{4}{3}\pi R^3 N_0 \quad (10.24)$$

Substituting N_0 from equation (10.24) in equation (10.23) we get $t_{1/2}$ in volume fraction.

$$t_{1/2} \propto \frac{R^3}{\phi_v}$$

Module 8: "Stability of Colloids"

Lecture 39: ""

The graph shows how the half-life decreases with size and concentration. (For a given volume fraction the number increases as the size decreases.)

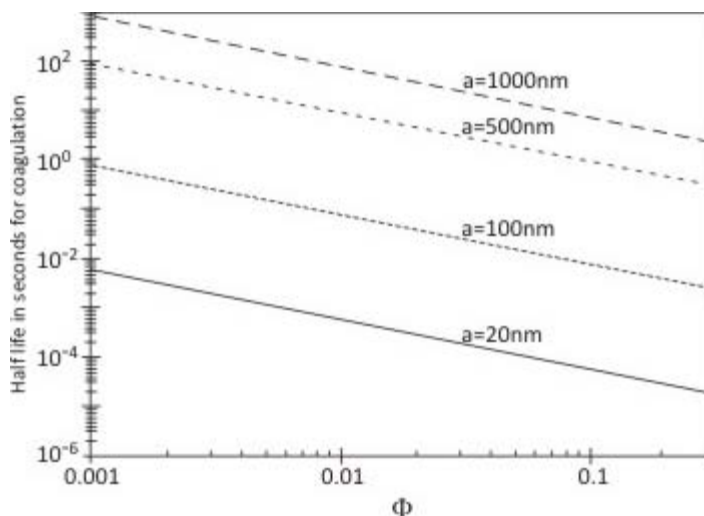


Fig.10.10: Half life of coagulation vs volume fraction for different particles sizes (a).

Radius of colloidal particle is of the order of $1\mu\text{m}$. Thus $N_o \approx 2.5 \times 10^{11} \phi_v$ and $t_{1/2} = 10^{11} / N_o$. This is an idea for the time required for rapid coagulation.

The simple Smoluchowski approach has its short-comings and limitations. The process of coagulation is described as the annihilation of particles by diffusion-controlled collision with other particles, without consideration for different particle sizes. The practical reason for this approach was that at that time data (Zsigmondy's study) only contained numbers of particles without discrimination with respect to size. Another problem is that only doublet formation is counted and further formation of doublets and triplets etc is not considered. Smoluchowski recognized this and formulated a more general treatment of evolving multiplet formation later.