Michael Faraday gold sol (1857)

A glass flask containing a suspension of nanoscale Au colloidal particles in water produced by Michael Faraday. The synthesis and optical properties of such colloidal suspensions and of beaten Au leaf were discussed in the famous Bakerian Lecture written by Michael Faraday in 1857. Au colloids were typically prepared using aqueous solutions of Au-containing compounds, such as sodium chloroaurate (NaAuCl₄). The addition of a reducing solution, e.g. phosphorus in carbon disulfide in a two-phase system, would produce the ruby red liquid seen in this photograph. Although not visible in any optical microscope at the time, it was Turkevich who used electron microscopy to show that such a synthesis results in Au nanoparticles of a few to a few tens of nanometers. Reproduced with permission from the Royal Institution of Great Britain (© Paul Wilkinson).

Experimental determination of CCC

Measurement of the coagulation rate can be made in two ways:
**directly** – measuring the number of particles as a function of time by particle counting (best for large particles)
Practically: The simplest experiment is to make up a series of tubes with different electrolyte concentrations and observe at which concentration aggregation becomes apparent after, say, 5 or 10 minutes. It can be quantified if the tubes are lightly centrifuged and a spectrophotometer is used to measure the percent transmission of the supernatant as a measure of the number of particles in suspension.

At higher electrolyte concentrations the rate increases to the plateau value, representing the fast or diffusion-limited rate.

**indirectly** – by light scattering (best for small particles).
In each case we are observing the change in the number of aggregates with time.
→ loss of primary particles from the system
Theory of coagulation

The higher $U_{\text{max}}$, the lower the probability of coagulation → coagulation rate slow
if the rate sufficiently slow (barrier high), the system can remain (kinetically) stable for years.
Rate increases with barrier reduction and coagulation becomes faster

Very important feature: secondary minimum at long separation distance (dependent upon...?)
Deep enough (several $k_B T$) to afford weak flocculation → gel (reversible by shear or peptisation → sol)

sol↔gel transition: thixotropy (reversible time dependence of viscosity)
Theory of coagulation

Kinetic stability of colloids in terms of interaction potential

Coagulation stepwise process:
1. Transport of particles toward each other (driving forces: external flow of carrier fluids, differential sedimentation, magnetic or electric fields, diffusion, repulsion/attraction)
2. Eventual attachment on contact, aggregation

   1. If diffusion prevailing transport mechanisms: perikinetic coagulation
   2. If velocity gradient: orthokinetic coagulation
Fuchs stability ratio $W$

Stability of a dispersion against coagulation quantitatively described as *stability ratio* $W$

$$W = \frac{\text{Rate of diffusion-controlled interparticle collisions (} k_0 \text{)}}{\text{Rate of interaction-force-controlled interparticle collisions (} k \text{)}}$$

$Über die Stabilität und Aufladung der Aerosole$

N.A. Fuchs, Z. Phys., 89 (1934) 736

Cosgrove, Colloid Science

Hiemenz, Principles of Colloid Chemistry

$$W = \frac{\text{Number of collisions between particles}}{\text{Number of collisions between particles that result in coagulation}}$$

R. J. Hunter, Foundations of Colloid Science

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Stability ratio $W$

$$W = \frac{\text{Rate of diffusion-controlled interparticle collisions (fast)}}{\text{Rate of interaction-force-controlled interparticle collisions (slow)}}$$

Numerator: rate in the absence of an energy barrier  
Denominator: rate in the presence of an energy barrier  
Assumption: collision between two particles leads to permanent contact between the colliding particles:

- Diffusion-controlled: **rapid** coagulation (Brownian motion always present)  
- Interaction forces-controlled: **slow** coagulation

Large values of $W \rightarrow$ system slow to coagulate $\rightarrow$ stable  
values of $W \approx 1 \rightarrow$ dispersion coagulates rapidly  
$W > 10^5$ with quite low potential barriers $\approx 15 \ k_B T$
Stability ratio $W$

$$W = \frac{\text{Rate of diffusion-controlled interparticle collisions (fast)}}{\text{Rate of interaction-force-controlled interparticle collisions (slow)}}$$

To a good approximation the **reaction-limited diffusion rate constant** is proportional to the Boltzmann factor which gives the fraction of particles at any instant with energy in excess of the primary maximum. The rate of aggregation drops rapidly with the **increase in the energy barrier**.

10 to 20 $k_B T$: **reasonable kinetic stability**
Experimental determination of CCC

Rate of coagulation against salt concentration indicating the critical coagulation concentration CCC

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Stability ratio $W$

\[ W = \frac{\text{Rate of diffusion-controlled interparticle collisions}}{\text{Rate of interaction-force-controlled interparticle collisions}} \]

- Rate of coagulation ($R_f$) in absence of potential barrier is limited only by the rate of diffusion: domain of fast/rapid coagulation

→ determine quantitative relation between $W$ and potential barrier:
- develop equation for rapid coagulation (theory of rapid coagulation)
- modify the equation to account for effect of interparticles energies (theory of slow coagulation)
Theory of rapid (r) coagulation

In absence of repulsive barrier
Assumptions:
1. no interparticle forces contributing to transport of particles toward each other
2. sufficient attraction to form a permanent bond upon contact
3. motion governed only by Brownian motion
4. collision probability scaled by \( \frac{1}{2} \)
5. Identical particles having same radius

The rate of fast coagulation \( k_0 \) was calculated by von Smoluchowski, who considered the process to be diffusion controlled. No interaction occurs between two colliding particles occurs until they come into contact, whereby they adhere irreversibly.

The number of particles \( N \) per unit volume after time \( t \) is related to the initial number \( N_0 \) by a second-order type of equation (assuming binary collisions \( \rightarrow \) dilute dispersion):

\[
- \frac{d[N]}{dt} = k_r [N]^2 \rightarrow \frac{1}{N} - \frac{1}{N_0} = k_r t
\]

\( k_r = 8\pi D R \) (identical particles)

N = final concentration
D = diffusion coefficient
R = radius


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Theory of rapid \((r)\) coagulation

\[
- \frac{d[N]}{dt} = k_r [N]^2 \rightarrow \frac{1}{N} - \frac{1}{N_0} = k_r t \rightarrow N = \frac{N_0}{1 + k_r N_0 t}
\]

Furthermore, since

\[
D = \frac{k_B T}{6\pi \eta R} \quad \text{and} \quad k_r = 8\pi DR
\]

Diffusion-controlled collision and coagulation

rate constant of coagulation of identical sphere particles depends only on viscosity and not on radius

(Valid for molecules, big/small particles)

Particles in aqueous dispersion at 25°C \(k_r \approx 6 \times 10^{-19} \text{ m}^3/\text{s}\)

1 Poise = 1 g/cm*s = kg/m*s
1 cP = 0.01 Poise
Water at 25°C 0.89 cP
Theory of rapid \( (r) \) coagulation

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THE VISCOSITY OF WATER 0°C TO 100°C

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<th>( \eta (cp) )</th>
<th>°C</th>
<th>( \eta (cp) )</th>
<th>°C</th>
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The above table was calculated from the following empirical relationships derived from measurements in viscometers calibrated with water at 20°C (and one atmosphere), modified to agree with the currently accepted value for the viscosity at 20°C of 1.002 cp:

\[
0^\circ \text{C} \text{ to } 20^\circ \text{C}: \log_{10} \eta = \frac{1301}{998.333 + 8.1855(T-20) + 0.00585(T-20)^2} - 1.30233
\]

(R. C. Hardy and R. L. Cottingham, J. Res. NBS 42, 573 (1949).)

\[
20^\circ \text{C} \text{ to } 100^\circ \text{C}: \log_{10} \eta = \frac{1.3272(20-T) - 0.06105(20-T)^2}{T + 105}
\]

(J. F. Swindelis, NBS, unpublished results.)

Viscosity (\( \eta \)) - The proportionality factor between shear rate and shear stress, defined through the equation \( F = \eta A \frac{dv}{dx} \), where \( F \) is the tangential force required to move a planar surface of area \( A \) at velocity \( v \) relative to a parallel surface separated from the first by a distance \( x \). Sometimes called dynamic or absolute viscosity. The term kinematic viscosity (symbol \( \nu \)) is defined as \( \eta \) divided by the mass density.

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CRC Handbook of Chemistry and Physics
69TH Edition
1986—1989
Theory of slow (s) coagulation

When there is an energy barrier to prevent the particles coming together the rate is slowed, as only a fraction of the particles collide with sufficient energy to exceed the height of the barrier and stick. **reaction-limited aggregation** with a rate constant $k_s$ in contrast to the diffusion-limited rate constant $k_r$. 

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Theory of slow (s) coagulation

whereas attractive forces can enhance collision rates and cause more rapid coagulation, energy barriers ($\Phi_{max}$ height of the barrier, net repulsive forces) instead reduce collision rates $\rightarrow$ slow coagulation

**Fuchs theory of slow coagulation**

Correlation between $W$ and height of the barrier in the approach of two particles of radius $R$ at distance $h$:

$$W = 2R \int_{2R}^{\infty} \exp \left( \frac{\Phi_{max}}{k_B T} \right) h^{-2} dh$$

*Über die Stabilität und Aufladung der Aerosole*

N.A. Fuchs, Z. Phys., 89 (1934) 736

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Theory of slow (s) coagulation

\[ W = 2R \int_{2R}^{\infty} \exp \left( \frac{\Phi_{\text{max}}}{k_B T} \right) h^{-2} dh \]

Evaluation of \( W \) as a function of:
- pH
- Electrolyte concentration
- Surface potential
- Hamaker constant
- \( a = \) radius of particles (identical)

When the \( \Phi_{\text{max}} \) height of the barrier large \( \approx 15 k_B T \)

\[ W = \frac{1}{2 \kappa a} \exp \left( \frac{\Phi_{\text{max}}}{k_B T} \right) \]
\[ t_{1/2} = \frac{3\eta}{4k_B T N_p} \]

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Theory of slow (s) coagulation

Half-life for coagulation of a series of dispersions of different particle sizes as a function of volume fraction: from top to bottom, 1000 nm, 500 nm, 100 nm and 20 nm radius

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Stability ratio $W$ and CCC

How the stability ratio $W$ varies with electrolyte concentration according to DLVO theory
$W$ experimentally determined by studies of rate of coagulation

$$\log_{10} W = K_1 \log_{10} c + K_2$$

$K_1 =$ constant (depending on surface potential, valence) it is **NEGATIVE**
$c =$ concentration of ions in solution

Stability ratio decreases with addition of the electrolyte until the electrolyte reaches a critical value above which the energy barrier between approaching particles disappears and $W$ becomes 1 (CCC)
Experimental determination of CCC

Rate of coagulation against salt concentration indicating the critical coagulation concentration CCC

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Stability ratio $W$ and CCC

$$\log_{10} W = -K_1 \log_{10} c + K_2$$

plot of $W$ for AgI sols coagulated with different electrolytes

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Stability ratio $W$ and CCC

1. Plot of $\log W$ vs $\log c$ is linear
2. Concentration at which $W = 1$ (curve breaks) measure the CCC of the involved electrolyte
3. Slow coagulation observed for $\log W < 4$ and for $W \approx 10^4$ (corresponding to $\approx 15 k_B T$)

$\rightarrow \approx 15 k_B T$ energy barrier required for appreciable stability
$\rightarrow$ if secondary minimum $\leq \approx 15 k_B T$ particles escape from it (peptization)
The Theory of Peptization, Wilder D. Bancroft

Peptization consists in the disintegration of particles so that they form a colloidal solution. We get a permanent colloidal solution whenever the particles are small enough to be kept in suspension by the Brownian movements and in some way are prevented from coalescing. Freundlich has postulated that all adsorption is accompanied by a lowering of the surface tension of the adsorbing phase. The theoretical deduction is unsound because the Gibbs theorem applies explicitly to true solutions and not to suspensions. On the
**deflocculation/peptization**

**deflocculation (peptization)**
The reversal of coagulation or flocculation, i.e. the dispersion of aggregates to form a colloidally stable suspension or emulsion.

http://goldbook.iupac.org/D01555.html

![Diagram of deflocculation/peptization](Image)

Precipitate of Fe(OH)$_3$

From electrolyte FeCl$_3$

Colloidal particles of Fe(OH)$_3$
deflocculation/peptization

deflocculation (peptization): used also as synthesis (dispersion) method

Ruling phenomena: adsorption of 1) single solvent; 2) mixed solvents; 3) non electrolytes; 4) ions; Resulting from preferential adsorption of common cations or protons

Steps:
1. Obtain a precipitate in order to achieve an agglomerate of colloidally dispersed particles
2. Washing, preferably by the aid of centrifuge
3. Adding an electrolyte which peptizes the mass, giving a sol in which the particles are positively or negatively charged as a result of a stronger adsorbtion of one ion with respect to the other
4. Dialyzing to remove excess electrolyte

Dialysis: purification process with membranes to remove low molecular weight salts or non electrolytes from colloids
Peptization is used also in nanoparticle synthesis (dispersion methods) to make a large grouping of particles split into many primary particles. This is done by changing the surface properties, applying a charge, or by adding a surfactant.

Example

In the synthesis of titania (titanium dioxide) nanoparticles, **peptization** involves adsorption of quaternary ammonium cation on the titania surface. This causes the surface to become positively charged. Electrostatic repulsion of the primary particles in the agglomerated titania breaks up the agglomerate into primary particles.
Peptization Mechanism of Boehmite and Its Effect on the Preparation of a Fluid Catalytic Cracking Catalyst

Yongsheng Zheng,† Jiaqing Song,*† Xiangyu Xu,† Mingyuan He,* Qian Wang,§ and Lijun Yan§

Figure 2. TEM pictures of colloid particles at acid/alumina molar ratios of (a) 0, (b) 0.02, and (c) 0.11.

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deflocculation/peptization

A boehmite colloid was prepared through peptization of boehmite with hydrochloric acid, and its particle size distribution was characterized during peptization. With an increase of the acid/alumina molar ratio from 0 to 0.11, the particle size of the boehmite colloid decreased to 3.5 nm. The particle size increased from 3.5 to 11 nm when the acid/alumina molar ratio was further increased to 0.16 and remained at 10 nm thereafter.

Proposed mechanism: With HCl added, the secondary boehmite particles absorb protons and repulse each other because of electrostatic repulsion force. The higher the acid/alumina molar ratio is, the smaller the dispersed particles are. The absorption of protons on the particle surface causes a decreased proton concentration inside the dispersed or boehmite particle. The boehmite particles were dispersed by the electrostatic repulsion between the protons on their surface absorbing to the surface hydroxyl groups. When a high acid/alumina ratio is used, the high concentration of anion from the acid can cause boehmite particle aggregation.