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A Thermodynamic Theory of Suspension I. Thermodynamic Theory

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The stability of a colloid has been treated in terms of repulsion by electric charge and attraction by cohesion of particles, but colloid particles are v-times larger in volume-size than the solvent molecules. v is as large as 10^{3-6} and the molar energy of cohesion H/v is negligibly small compared with the electric repulsion energy W_{el}/v. Cohesion acts over the distance of 1—5 Å or only at the contact point. H does not increase with v, contrary to the DLVO theory. The molar energy of sedimentation W_{sed}/v is taken as an influential factor for the stability of a colloid of large particles. It is calculated from Stokes law as $W_{sed}/v = \Delta\rho u^2$, where $\Delta\rho$ is the density difference and u is the stationary velocity of sedimentation equal to $(\Delta\rho/\eta)(2/9)gr^2$, where η, r, and g are viscosity of solvent, radius of particle, and acceleration constant of gravity, respectively. Sedimentation occurs when W_{sed}/v is equal to $kT/3$, i.e., the perpendicular component of the energy of Brownian motion. The critical radius r_c is $r_c = 30C\,\text{nm}$, where $C = 10\,(\eta^2/\Delta\rho^3)^{1/4}$ and k is Boltzmann's constant. r_c is 10—100 nm for inorganic sol, above 100 nm for organosol and aerosol. A theory of colloidal solution is proposed by using a lattice model of size v. Molar free energy of mixing ΔG of the volume fraction of particles ϕ is $\Delta G = [(1-\phi)\ln(1-\phi)+(\phi/v)\ln(\phi/v)]RT+(\phi W_{sed}-\phi^2 W_{el}+\phi^2 H)/v$. Solubility is $\phi = [1-(r/r_c)]/[1+(1/v^2)+(H-W_{el})/vRT]$. W_{sed} is absorbed internally in the dispersion system. When $r > r_c$, sedimentation takes place to form muddy mixtures including agglomerates of particles. Cohesion acts only at a contact point and is negligibly small.

A colloid is a mixture of particles and solvent molecules. A colloid is liquid-like similar to a molecular solution in spite of the extremely large sizes of its particles. The relative radius r of particles is 10—100 times or relative volume v is 10^3—10^6 times larger than solvent molecules.

At the present time, the stability of colloid is treated usually by hydromechanics, the balance of forces being taken into consideration. Cohesion and electric force of charged particles act as forces of attraction and repulsion, respectively.[1] However, electric repulsion is inversely proportional to the distance d between particles, whereas cohesion is proportional to $1/d^6$. Cohesion is too small to act in a dispersion except for the coagulated state, where cohesion acts only at contact points and is very small.

Nevertheless, cohesion has been estimated to be large enough according to the theory of Derjaguin–Landau–Verwey–Overbeek (DLVO)[1,1a,2] and Hamaker.[3] They calculated the cohesion energy between particles based on an assumption that molecules existing inside of a particle interact with those inside other particles in a vacuum, but this assumption seems to be too far from reality, as discussed later. However, some attraction term other than cohesion is necessary for a balance with the mixing entropy and also with electric repulsion for particles of the same electrical charge.

On the other hand, in thermodynamics the stability of the mixture is dealt with in terms of the change in the free energy or the energy and entropy of mixing. In fact, for ordinary and polymer solutions, the mixing energy is taken to be the cohesion energies among solute and solvent molecules contacting with each other, and the change in the free energy of mixing is calculated by using a small cell of the same size for the solvent molecules in the lattice model.

Large paricles in a colloid possess a molar volume v -times larger than that of solvent, but the number of contact points with other particles is one per particle. Therefore, for particles of the size v and volume fraction ϕ, the molar concentration of particles in the unit volume of the mixture is ϕ/v. Actually, the effect of molar heat of cohesion H is proportional to ϕ^2 (H/v) and it is negligibly small for large particles. The molar volume of a molecule is V_0 and its cohesion heat is H, whereas those of a particle are vV_0 and H, because H acts at the contact points without increasing with v.

On the other hand, the molar energy of gravity difference of particles with solvent molecules is large enough and increases as v increases. The present author takes the gravity energy of particles into consideration and constructs a thermodynamics of suspension, by expressing the stability as a function of free energy of mixing composed of entropy of mixing and energy of gravity. The necessity of thermodynamical concepts was somewhat recognized already by several authors.[1]

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Alder[1b] suggested a phase-transition occuring at a ϕ of 0.5 from the calculation at the equilibrium state of sedimentation. In fact, transitions were observed not only for a rod-like colloid, e.g. tobacco-mosaic virus, but also for spherical paricles. In the state of phase separation, the particles of polystyrene form an ordered structure like a crystal.[1]

Onsager calculated the transition and found that it occurs at a ϕ of 2.3% which is compatible with the experimental value i.e. 2.5%.[1c] It was assumed that a rod-like particle behaves as a rotating disk and he calculated the transition as it is caused by cohesion. In these works, cohesion is also taken as the attraction term.

The thermodynamic theory of suspension is still insufficient at the present. In the dynamic state, the mixture of particles and solvent molecules are in a liquid state due to Brownian motion of particles. The size of particles affects the degree of the Brownian motion per volume and changes the entropy and energy of mixing. The author proposes a thermodynamics of colloidal dispersion by taking the energy of gravity of particles into consideration.

Theory

Notation Used Often in This Article. Subindex "0" denotes solvent used in necessary cases. V and V_0 are the molar volumes of particle and solvent molecule and v and r are the ratio of volumes and that of radius, or V/V_0. v and r are also often used for the ratio of volume and radius of particles to those of solvent molecules. ϕ is volume fraction of particles. Molar concentation of paticles per unit volume is ϕ/v and that of solvent is $1-\phi$. N_A is Avogadro's number, 6×10^{23} per mol and N is $N = N_A/V_0$ per volume of the specimen. h is Planck's constant, 6.6×10^{-27} erg s.$^{-1}$ k is Boltzmann's constant, 1.3×10^{-16} erg deg^{-1} K. $R = kN_A$: gas constant, 2 cal K^{-1}. 1 cal = 4.184 J, erg = 10^{-1} J, J (Joule) = 0.1 kg m = 10^7 g cm. T is absolute temperature K. H is molar cohesion heat in cal. It is exothermic and have a negative value. ΔH_m is heat of mixing; positive value in ordinary cases, when no hydrogen-bonding nor chemical reaction occurs. W_{sed} is molar energy of sedimentation of particles. W_{el} is molar energy of electric repulsion according to Debye–Hückel.

1. Thermodynamic Concept of Suspension. A suspension is a kind of mixture composed of particles as solutes and solvent molecules and resembles a molecular solution. A suspension is also liquid-like in the dynamic state due to the Brownian motion of particles and solvent molecules, although the diameters of spherical particles are 10 to 100 nm and are extremely large compared with that of ordinary molecules, i.e., several Å. A suspension of large particles is obtained by vigorous agitation and it is muddy and of higher viscosity than the solvent alone.

According to Einstein–Stokes theory, the square mean distance $\bar{x}^2$ of the fluctuation in the Brownian motion of particles decreases as the radius of particle increases. Such motion is called the micro-Brownian motion. For the same reason, the diffusion constant of particles decreases as the radius of particles increases. These behaviors as well as the stability of colloid may be explained in terms of kinetics as well as thermodynamics of solution more simply than in terms of mechanics.

Thermodynamically, the stability is expressed by the change in the Gibbs free energy of mixing in the unit volume of the mixture ΔG_m, which is composed of the heat of mixing ΔH_m and the entropy of mixing ΔS_m as

$$\Delta G_m = \Delta H_m - T\Delta S_m. \tag{1}$$

Spontaneous changes in the dynamic state tend to proceed so as to decrease ΔG_m and to increase ΔS_m. ΔH_m and ΔS_m are calculated by means of the lattice model. In the dynamic condition, the configurations of particles and solvent molecules change dynamically and the probability of existence of the various states is proportional to a product of the number of configurations times the multiplicity expressed by an exponential function of the energy of each state according to Boltzmann. For the suspension of particles, the lattice of large cells is to be employed, which is almost equal to the volume of a particle. The effect of size on the stability of suspension is expressed as functions of molar concentrations of particles and solvent molecules.

Colligative properties of the mixture are expressed in terms of the molar concentrations per a unit volume of the mixture, which are affected by the size of particles. We use the subindex "0" for solvent; then the molar concentrations per a unit volume of the mixture are ϕ_0/V_0 and ϕ/V, where V_0 and V are their molar volumes, respectively. V/V_0 is v i.e. the relative degree in size. Molar concentrations of both species are $(1-\phi)$ and (ϕ/v) and different from volume concentration i.e., $(1-\phi)$ and ϕ, respectively. As a result, the latter is very small in a colloidal solution.

2. Lattice Model for Suspension. In the ordinary lattice model, each cell contains a solute or a solvent molecule of almost the same size. Molecules possess Brownian motion in each cell and there must be some free volume in the dynamic state. A volume of cell is taken to be somewhat larger than the volume of a molecule.

The kinetic energy for the translational motion of a molecule is kT or a molar energy RT. For an ordinary molecule the free volume is about 10% of the molecular volume. When it becomes 2.5%, Brownian motion is almost lost and the state becomes solid by cohesion into glass or crystal (See Appendix).

For particles the molar kinetic energy is RT, but their Brownian motion is slow due to the large size and is called the micro-Brownian motion. For the suspension, the lattice composed of v-sized cells is to be employed which can contain a particle or v solvent molecules, because by the ordinary lattice of v of 1, the spaces between 1 and v fall out of the calculation of configurations.

3. Energy of Cohesion and Electric Repulsion. For an ordinary solution, ΔH_m has been calculated from the interaction energy between particles [2-2], solvent molecules [1-1] and particle-solvent [1-2] and [2-1]. Therefore, ΔH_m is expressed in terms of the ratio of molar cohesion heats H_i

to the molar volumes V_i or in terms of solubility parameters δ_i, i being the components 1 or 2. Cohesion is an exothermic phenomenon and H_i have negative values. Then, ΔH_m becomes[5]

$$\Delta H_m/V_{12} = 2[(H_1H_2)/(V_1V_2)]^{1/2} - (H_1/V_1 + H_2/V_2) = (\delta_1 - \delta_2)^2. \tag{2}$$

where δ_i is $(-H_i/V_i)^{1/2}$ and is called the solubility parameter. For a colloidal solution, V_2 and V_{12} are very large and δ_2 becomes $\delta_2/v^{0.5}$ and ΔH_m is

$$\Delta H_m/V_{12} = (\delta_1 - \delta_2/v^{0.5})^2. \tag{3}$$

For large particles ΔH_m may be small or nearly equal to zero, because cohesion acts only at the contact point of particles and the number of points is proportional to ϕ^2/v, whereas H_2 is not changed by v and is the same as that of molecules existing at the contact point and is not larger than that of a molecule. The cohesion term is

$$\phi^2(-zH_2/vRT) = (\phi^2/v)\chi, \tag{4}$$

where χ is $-zH_2/RT$, z being the coordination number of 8—10. The values for a particle in Eq. 4 are small.

The cohesion energy per unit volume of the suspension is negligibly small except for the interaction with the particle in the neighboring cells, for which the distance d between particles is 0.5 nm, because the free volume is about 10% of the molecular volume in ordinary cases and the radius of a molecule is about 1 nm and the radius of the free volume is $0.1^{1/3}$ nm or 0.46 nm. Therefore, the active distance of cohesion of a particle is smaller than 1 nm. It is called a van der Waals radius of 0.1—0.5 nm.

In the theories of DLVO[2] and Hamaker,[3] the collision of particles induces cohesion when particles approach to the effective distance. The cohesion energy is $19kT$ according to the DLVO theory. It is very large compared with the values estimated from the concept of the lattice model, perhaps due to an unsuitable calculation in the DLVO theory which will be explained later.

For ordinary colloid, the radius lies between 0.01 and 1 μm and is very large compared with 1 nm of the solvent. v becomes 10^3—10^6 or more and the cohesion term is very small in the system of solution. This is also contrary to the theories of DLVO and Hamaker.

On the other hand, the electric repulsion of charged particles is inversely proportional to the distance d between particles and acts in wide and long ranges. In this case, the number of particles is ϕ/v and each particle possesses z_i ions. The electric repulsion energy W_{el} is

$$W_{el} = N_A z_i e^2/\varepsilon d, \tag{5}$$

where N_A is Avogadro number, e is the unit electric charge, and ε is the dielectric constant of the solvent. Thus, the electric term is very large and over the kinetic energy RT, contrary to the small cohesion term.

On the other hand, counter ions form an electric double layer which affects W_{el} according to Gouy[1,1d] and Chapman.[1,1e] The effect is expressed by Debye–Hückel[1,1f] and was involved in the DLVO theory. In any case, W_{el} is large enough for acting as a repulsion term in place of the entropy of mixing. Therefore, the dispersion of electrically charged particles is too stable to distiguish the effects of cohesion from that of gravity.

However, the calculation of H by the DLVO theory seems to be doubtful. The gravity effect has size effects on the properties of suspension and often gives muddy agglomerates. For non-charged particles of uniform size, an ordered structure like a crystal is formed, which involves a domain of void filled with solvent. It may be explained by the partial sedimentation. Orientation of particles may take place by partial sedimentation, as will be discussed in Part II.

4. Energy of Gravity. As another energy term of particles, the author takes the energy of sedimentation into consideration. For large particles, sedimentation occurs, but particles are incorporated in the suspension system by vigorous agitation. For small particles, sedimentation does not occur in average but locally it may occur, the effect disappears by the compensation by the kinetic energy of Brownian motion of solvent molecles. The transfer of kinetic energy between particles and solvent molecules is a rate process and more or less affects the uniformity as well as the stability of the suspension.

The energy of sedimentation or gravity W_{sed} acts as an energy term similarly to the cohesion of particles. It acts in one-dimension and the molar energy of gravity per unit volume is

$$W_{sed}/v = (\rho - \rho_0)u^2/3. \tag{6}$$

Here, ρ and ρ_0 are the densities given in g cm^{-3} of particles and solvent, respectively. $(\rho - \rho_0)$ is denoted $\Delta\rho$. u is the falling velocity of particles given in cm s^{-1} and increases with time t but becomes constant in the stationary state by the balance between the sedimentation force of particles and the viscous resistance of the solvent. The stationary velocity is obtained by using the Stokes law as

$$u = \Delta\rho g v/6\pi\eta_0 r = (\Delta\rho/\eta_0)(2/9)gr^2, \tag{7}$$

where g is the acceleration of gravity, i.e., 980 cm s^{-2} and η_0 is the viscosity of the solvent of 10^{-2}—10^{-3} poise or 10^{-3}—10^{-4} Pa s.

The critical value for W_{sed} at room temperature is

$$W_c/v_c = \Delta\rho u^2/3 = kT/3 \quad \text{or} \quad \text{at } T \text{ of } 300\text{ K} \tag{8}$$

and

$$\rho u^2 x\ (\text{cm}^3\,\text{g}^{-1}) = \Delta\rho\{(\Delta\rho/\eta_0)(2/9)g\}^2 r^4\ (\text{cm}^3\,\text{g}^{-1}) = kT/3 = (300/3)1.3 \times 10^{-16}\ \text{dyne cm mole}^{-1}. \tag{9}$$

The critical radius r_c at 300 K is

$$r_c = [(300 \times 130 \times 10^{-16}/\Delta\rho)/\{(\Delta\rho/\eta_0)(2/9)g\}^2]^{1/4} = 0.3 \times 10^{-4}[\eta_0{}^2/\Delta\rho^3\ (\text{g cm}^{-1})]^{1/4}\ \text{cm} = 30C\ \text{nm}, \tag{10}$$

where C is a factor expressed in cgs-units as

$$C = 10[\eta_0{}^2/\Delta\rho^3\ (\mathrm{g\,cm^{-1}})]^{1/4}. \tag{11}$$

For an aqueous suspension, η_0 is 1 centipoise or 1 mPa s and ρ_0 is 1 g cm^{-3}. ρ is given in g cm^{-3}.e.g., 1.05 (polystyrene), 3 (cement paste), and 5 (metal suspension) and r_c given in nm is 280, 18, and 11, respectively. Roughly speaking, 100 nm is a border line between organo and inorganic colloids. For organosol, particles lighter than solvent induce flocculation.

For the critcal volume v_c or $r_c{}^3$, W is proportional to $r_c{}^4$ for spherical particles and $N_A k$ is the gas constant R. At the critical point

$$W_c/v_c RT = 1. \tag{12}$$

Above v_c, agitation is necessary to maintain the state of dispersion. Otherwise, sedimentation occurs.

5. Micro-Brownian Motion. The effect of gravity of particles is derived from the concept of Brownian motion, which was already established in the classical theory of colloids.[1a] The irregular motion of a pollen particle was observed in water by R. Brown. As the origin of the Brownian motion, Langevin, Einstein and Stokes[1] assumed that the energy of the colloidal system is composed of random motion of solvent molecules and particles F, and the frictional motion of particles and solvents f (dx/dt). The total energy of a particle having a mass m is constant in the stationary condition or m (d^2x/dt^2) of zero and

$$m(\mathrm{d}^2x/\mathrm{d}t^2) = F + f(\mathrm{d}x/\mathrm{d}t), \tag{13}$$

The kinetic energy F is distributed between particles and solvents but the average value is not different between them, and the squared-average velocity $(\mathrm{d}\bar{x}/\mathrm{d}t)^2$ is equal to $kT/2$. Since the volume of a particle is very large compared with the values of a solvent molecule, the motion of particles is very slow and is called the micro-Brownian motion.

F is negative, whereas f(dx/dt) is positive and the total kinetic energy of particles is zero. As a result, the amplitude of the fluctuation of random motions is

$$\mathrm{d}x^2/\mathrm{d}t = kT/f \quad \text{or} \quad x^2 = 2kTt/f. \tag{14}$$

The frictional coefficient f is inversely proportional to diffusion constant D according to the Stokes relation as

$$f = 6\pi r\eta_0 = kT/D, \quad \text{or} \quad D = kT/6\pi r\eta_0. \tag{15}$$

Thus, the Brownian motion decreases as the radius increases.

The sedimentation is caused by the effect of gravity provided from the outside. For suspension of small particles the effect of gravity may vanish through the process of the exhange of the kinetic energy of the Brownian motion of particles and solvent molecules ; the partial sedimentation may occur and decrease the micro-Brownian motion of particles. It is recovered at the expense of the Brownian motion of solvent molecules, resulting in the decrease in the temperature of solvent molecules, but it is compensated by the frictional heat of particles with solvent, respectively. The balance of change in the entropy and energy is important for the equilibrium condition.

The particles larger than the critical size tend to induce sedimentation, but the process is very slow due to the slow Brownian motion. For example, cement particles are of radii of several μm larger than its critical value i.e. 30 nm. The viscosity of cement paste increases but gradually for a considerable time before coagulation. According to Eq. 15 diffusion coefficients are inversely proportional to the radius of particle and the translational velocity of particles is not so large as to induce collision of particles in colloids. These problems are discussed in Part II.

6. Thermodynamics of Colloidal Solution. In a molecular solution the solute and solvent are of almost the same size and the change in Gibbs molar free energy of the mixture per unit volume ΔG_m is calculated easily.

At the constant temperature T and in the constant volume of the solution, ΔG_m is expressed by two terms: the entropy term $-T\Delta S_m$ and the heat of mixing ΔH_m.

In the lattice model ΔS_m is concerned with the displacement of molecules of solvent 1 by solute 2 in the lattice and has been calculated already.[5,6] For N_1 solvent molecules and N_2 solute molecules, the number of displacements is given as

$$(N_1 + N_2)!/N_1!N_2! = 1/\phi_1{}^{\phi_1}\phi_2{}^{\phi_2},$$

whereas that before mixing is 1. ΔS_m is given as

$$\Delta S_m = -R[\phi_1 \ln \phi_1 + \phi_2 \ln \phi_2], \tag{16}$$

In the case of a polymer, a chain molecule is composed of n segments and the chain is flexible. The number of configurational changes is affected by n and the coordination number z as

$$\Delta S_m = -R[\phi_1 \ln \phi_1 + (\phi_2/n)\ln \phi_2 - (n-1)\ln (z-1)/e]. \tag{16a}$$

However, for a suspension, particles are extremely large as compared with solvent molecules and the calculation of mixing entropy is not yet proposed. In this case, the v-sized lattice may be taken, the number of which is N/v per unit volume,1 cm^3. The displacement of particles should be done first in the lattice of the number of ϕ_2/v, and then v solvent molecules are inserted into the empty lattice. Then the free energy change per unit volume of suspension is

$$\Delta G_m = [(1-\phi)\ln (1-\phi) + (\phi/v)\ln (\phi/v)]RT + (\phi W_{\mathrm{sed}} - \phi^2 W_{\mathrm{el}} + \phi^2 H)/vRT. \tag{17}$$

Solubility or concentration of particle in the equilibrium is given by the condition that

$$\mathrm{d}\Delta G_m/\mathrm{d}\phi = 0 \text{ and } \quad W/vRT = r/r_c$$

as

$$\phi = [1 - (r/r_c)]/[1 + (1/v^2) + 2(H - W_{\mathrm{el}})/vRT], \tag{18}$$

which holds only for the case that $r < r_c$ and $W_{\mathrm{el}} < (RT/2) + H$. For large particles sedimentation occurs and for charged particles no coagulation occurs, unless a salt of a strong acid is added.

7. Role of Critical Radius. The critical radius r_c is important for thermodynamics of colloidal solution. The energy of sedimentation is a mechanical energy and is often caused by the small turbulence occurring on the occasion of the preparation, formation or measurement of viscosity of colloids. For particles of size less than r_c, the sedimentation energy is absorbed by the homogeneous system of solution through the friction of particles with the solvent. This is the internal sedimentation.

In relation to the phase transition in solution, a pure liquid possesses two transition temperatures, temperatures of boiling T_b and of melting T_m. Above T_b the state is gaseous where molecules collide violently, whereas below T_m it is solid without translational motion. In the liquid state the Brownian motion occurs and its degree depends on temperature. Free volume is necessary for Brownian motion and for an ordinary liquid it is usually 10% of that of a liquid, whereas it is 2.5% at the glass-transition temperature T_g. For a polymer there are viscoelastic states between T_m and T_g (See Appendix).

8. Aerosol. An aerosol is composed of small particles of mist, smoke or smog dispersed in gaseous media. In dynamic or liquid state of suspension, Eq. 10 can be applied. The media is air and η_0 is very small as 18 μPa s. The difference in density $\rho - \rho_0$ or $\Delta\rho$ is almost equal to ρ. The factor C for ρ of 1 is $(\eta_0^{0.5}/\Delta\rho^{0.75}) = (18 \times 10^{-5})^{1/2}$ and the critical radius becomes :

$$r_c = 0.23 \times 10^{-4} \times C \text{ cm} = 0.5\ \mu m. \tag{19}$$

However, when vigorous agitation is provided to the suspension, the state becomes a gaseous state and collision of particles occurs. Agitation improves dispersion but sometimes induces coagulation by thixotropy for particles of liquid or low melting point polymers.

As a special case, water mist can vaporize and its particle size changes depending on atomospheric conditions.

9. Question to the Theories of DLVO[2] and Hamaker[3]. The van der Waals or London force is developed by cohesion and cohesion is caused by a temporary polarization due to the interaction of the neighboring molecules. The effective distance is inversely proportional to the sixth power of the distance of particles d in vacuum and it is limited to several Å. In thermodynamics, the cohesion heat acts only at the contact point or the coordination sites. However, de Boer and Hamaker calculated the cohesion energy of particles over a long distance d and expressed it to be

$$H \approx (-Ar/12d), \tag{20}$$

where A is Hamaker's constant and is equal to $(3/4)\pi^2 q^2 \alpha^2 h\omega$, where q, α, and $h\omega$ are density, polarizability, and energy of polarization, respectively. The cohesion energy thus calculated is regarded to act as the attraction term and it is proportional to $1/d$, similarly to the permanent dipole.

The calculation was based on the following assumptions; the polarization occurs in vacuum. Each molecule existing inside of a particle interacts with molecules in other particles and the interaction energy is proportional to $1/d^6$. Total dipole is obtained by summation and behaves as a permanent dipole. Then the calculated interaction energy acts over a long distance and the effect is proportional to $1/d$.

However, it is questionable to assume that the wave of interaction energy propagates through the inside of a solid particle similarly to the way it propagates in vacuum and so many waves of energy are synchronized like the permanent dipoles or ferromagnetism. Modification is later done between particles with use of dielectric constant of solvent, but not yet for the inside of particles. The present author can not agree with the theory. Any estimation of cohesion energy based on the DLVO theory seems to be over-estimated by a factor related to the size v of particles.

Measurement of the interaction energy has improved recently and the energy is found to be large enough, but it was measured for a precipitate. The effect of cohesion in the dynamic state is still obscure. Therefore, the problem of the origin of the attraction, cohesion or gravity in the dynamic state is not yet settled.

Conclusion

The author has proposed a new theory for stabilization of suspension of large particles from a viewpoint of thermodynamics. The free energy of mixing for particles and solvent molecules in colloid is expressed as a mixing entropy and an energy term of the gravity of particle in place of cohesion. This is different from the ordinary theories based on the balance between electric repulsion and cohesion heat. The molar energy of cohesion of particles is not larger than a molecule, contrary to the estimation according to the DLVO theory. Various states of colloid are explained by the total free energy of mixing including the mixing entropy as well as energy of gravity and electric repulsion.

Appendix

Empirical Rules and Assumptions. The theory of thermodynamics and kinetics is almost completed in an ordinary solution. But for explanation of colloidal properties several problems remain. The author proposed the following explanations or theories.

1. Thermodynamics. Thermodynamics deals with the equilibrium,[6] whereas kinetics deals with the rate processes. In thermodynamics there are three states: gas, liquid and solid. Molecules possess kinetic motion and one molecule's energy is kT or the molar energy is RT. For ideal gas, Boyle–Charles equation Eq. 21 holds as

$$pV = RT. \tag{21}$$

But actually, it must be modified by the effect of cohesion in the vicinity of a condensed state and the van der Waals equation Eq. 22 is applied as

$$(p + a/V^2)(V - b)RT. \tag{22}$$

There is a minimum and a maximum in the p–V relation and the critical temperature T_c.[6]

2 Kinetics for Rate Processes. The activation heat E^* for chemical processes is given by the difference in bond energies of molecules in the initial, final and the activated states. In the process: AB+C$\longrightarrow$A$\cdots$B$\cdots$C(activated state)$\rightarrow$A+BC, the bond energies D's are calculated as follows: As a simple case like cohesion of particles, D of the activated state is assumed to be $D_{[\mathrm{A}\cdots\mathrm{B}\cdots\mathrm{C}]} =$

$(D_{A-B}+D_{B-C}+D_{[A+B+C]})/3$ and D of the non-bonding state $D_{[A+B+C]}$ is zero.[7] Then, for substitution reaction

$$E^* = D_{A-B} - D_{[A\cdots B\cdots C]} = (2/3)D_{A-B} + (1/3)D_{B-C}.$$

For decomposition, where $D_{B-C} = 0$

$$E^* = (2/3)D_{A-B}. \tag{24}$$

For viscous flow, where $D_{A-B} = D_{B-C}$, the activation energy E^* of viscous flow is

$$E^* = (1/3)D_{A-B}. \tag{25}$$

Eyring[8] assumed that E^* is one-third or one-fourth of heat of vaporization H_{vap} of the liquid as

$$E^* = (1/3\text{—}1/4)H_{vap}. \tag{26}$$

3. Transition Points.[9] Transitions occur at the boiling point T_b and the melting point T_m. In the gaseous state the temperature T is high and molecules collide violently with each other. Below T_b, it becomes the liquid state, due to decreased temperature; the kinetic energy kT decreases but still large enough for Brownian motion in the liquid phase. The Brownian motion is limited to the inside of the free volume in the lattice model. Below T_m, Brownian motion is lost and the state becomes a solid or crystal but some times it is a super-cooled liquid or a glassy solid. The glass-transition point T_g is about two thirds of T_m.

In the thermodynamics the change in Gibbs free energy ΔG stored in the system is expressed by the heat absorbed ΔH and the increase in the entropy ΔS as

$$\Delta G = \Delta H - T\Delta S.$$

At the equilibrium, ΔG becomes the minimum or zero and the transition points are given as

$$T_b = \Delta H_b/\Delta S_b \tag{27}$$

and

$$T_m = \Delta H_m/\Delta S_m \tag{28}$$

In thermodynamics of solution, ΔH_b is the heat of vaporization ΔH_{vap} and T_b is two-thirds of the critical point T_c. However, transition is regarded as a rate process.

$$T_g = (2/3)T_m, \tag{29}$$

which is understandable from the concept that T_m is the thermodynamic equilibrium point, whereas T_g is the rheological point and

$$T_g = E^*/R, \tag{30}$$

$$T_m = H/R, \tag{31}$$

and according to Eq. 24

$$E^* = (2/3)H. \tag{32}$$

For a polymer, Eq. 29 is obtained from the relaxation times of pseudo links of small size A and a large size B.[9].

4. Free Volume. For free volume, Eyring[8] presented a theoretical equation derived from geometrical calculation

$$v_f^{1/3}H = RT. \tag{33}$$

But it gives no T_g nor v_{fg}. The present author[9] proposed from concept of the dynamic state

$$v_f H = R(T - T_g), \tag{34}$$

which gives v_f of 12.5—10% in liquid and at T_g

$$v_{fg} = R(T_m - T_g)/H = v_f(1 - T_g/T_m) = v_f/3 = 4.2\text{—}3.3\%. \tag{35}$$

Another derivation is possible.[10] According to the hole theory of Eyring, viscous flow needs a hole. It may be the sum of the free volume of the coordinated particles. The fraction of free volume relative to the volume of a molecule may be

$$v_f = 1/z = 1/8\text{—}1/10 = 12.5\text{—}10\% \quad \text{for } z \text{ of } 8\text{—}10, \tag{36}$$

For an amorphous solid, the displacement of the molecules is not regular but at random and the melting occurs at T_g. Glass forms at the final stage in the dynamic state. Coagulation by cohesion may be a rate process and slow unlike crystallization.

The process may be a kind of formation of clusters.[10] In the first step a particle is linked with one of the coordinated parices and its probability is $1/z$, but in the second step it may be $1/(z-1)$. As a result, for the second step the fraction of free volume is

$$v_{fg} = 2/z(z-1). \tag{37}$$

For z of 8—10, v_{fg} is 3.5—2.2%.

5. Thermal Expansion.[10] The above concept is extended to an explanation of thermal expansion coefficient α for polymer as

$$\alpha = 1/zT_g, \tag{38}$$

for z of 10 and T_g of 250 K

$$\alpha \approx 1/(10 \times 250) = 10^{-5}\ \text{deg}^{-1}.$$

Below T_g

$$\alpha_g = [2/(z-1)]\alpha = \alpha/4. \tag{39}$$

These relations hold for a polymer as well as an ordinary liquid.

6. Application to Suspension. The gaseous state of suspension is achieved by vigorous agitation, but the solvent phase does not expand nor do particles vaporize. The state corresponds to a critical state forming at high pressure. Collision of particles may occur but it is weak compared with the case of molecules. The normal state of a suspension is the liquid or dynamic state having no micro-Brownian motion of particles.

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