and then inoculated on aluminum foil, they failed to be sterilized with ethylene oxide. Likewise, *Bacillus subtilis* var. *niger* spores suspended in peptone and dried on aluminum foil with a contamination level of only 10 spores/carrier were very difficult to sterilize with ethylene oxide. This would be similar to the protective effect found by previous investigators (6), *i.e.*, occlusion of the spores in crystals.

It is also possible to produce artificial conditions which would seem to make the organisms extremely susceptible to ethylene oxide. Spores suspended in 2% glycerin and then dried on polystyrene were less resistant to ethylene oxide than spores suspended in distilled water (7). *Bacillus subtilis* var. *niger* spores were suspended in 10% glycerin, inoculated on chromatography paper strips, and dried at room temperature. After drying at room conditions, the glycerin will contain a certain amount of water depending on the room relative humidity, for it will gain or lose moisture depending on its surroundings. At 130°F., 1,200 mg./L. ethylene oxide, these strips showed the same resistance (3 min. for inactivation) at 40% RH as at 10% RH even though the strips at 40% RH would contain a greater amount of moisture after equilibration. A similar situation would indicate to the unwary that no optimum RH was required. However, clean spores inoculated from distilled water required 1 hr. at 10% RH and 3 min. at 40% RH for inactivation.

SUMMARY

The evaluation of the efficiency of an ethylene oxide process depends a great deal on the type of bacteriological control used. It is therefore recommended that an evaluation be made of the type of load to be sterilized, so that the bacteriological controls chosen will accurately monitor the process. If one uses unwashed spores for preparation of sterility monitors when sterilizing clean materials, then he will likely obtain erratic indications of nonsterility rather than sterility. If, however, one does attempt to sterilize dirty materials, contaminated with dirt, blood, feces, *etc.*, he must realize that the process at its best will sterilize occasionally and should only be considered a decontamination procedure. The only dependable method of testing a sterilization process is to determine if it kills living microorganisms. The microbial control chosen should simulate actual conditions of the materials being sterilized.

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◦⌐⟋ *Keyphrases*

Ethylene oxide sterilization
B. subtilis spores—ethylene oxide effect
Staph. aureus—ethylene oxide resistant
Sterilization, ethylene oxide—variables affecting

Preferential Aggregation and Coalescence in Heterodispersed Systems

By NORMAN F. H. HO and W. I. HIGUCHI

A theoretical study of preferential coalescence and aggregation of small particles in heterodispersed systems has been carried out where moderate electrical barriers exist between the particles. Equations based on the concepts of Derjaguin, Verwey, and Overbeek were employed. Computation over a wide range of conditions has shown that small particles may aggregate (or coalesce) with themselves or with larger particles at rates that are 10 to 50 orders of magnitude faster than particles 10 times larger. These findings may explain (*a*) the relatively narrow particle size distributions observed in certain emulsions and flocculated suspensions and (*b*) the limited flocculation and coalescence behavior observed in certain instances.

THERE ARE many situations involving suspensions and emulsions where with time the particles or droplets of the dispersed phase simultaneously increase in size and narrow in their relative size distributions, and then later became

quite stable kinetically. If the dispersed phase is soluble (or miscible) enough in the solvent, then the phenomenon may be accounted for by molecular diffusion (1) or Ostwald ripening. However, there are many examples in the literature (2–5) where the changes appear to occur primarily through particle–particle aggregation or droplet–droplet coalescence.

The authors have recently observed that urea-

denatured ovalbumin aggregates precipitated in buffered saline near the isoelectric point are often made up of rather uniform particles of around 1 μ diameter (2). Sherman (3) found that emulsions pass through an initial phase of rapid coalescence followed by a second period of slow coalescence, and then the emulsions became relatively stable. All of his emulsions showed a relatively narrow size distribution in the later stages. Wiley (4) and Gillespie (5) have also studied the problem of limited coalescence when droplets in oil-in-water emulsions are stabilized by finely divided particles.

Although the effects of particle size on the stability of colloids have been recognized, quantitation has been limited to the case involving the potential energy barriers for particles of equal sizes (6) or for particles of different sizes in which the mean size is used (3). While the equations for the repulsive potential energy between two unequal spheres have already been derived, an expression for the attractive potential energy between two unequal spheres with retardation factors has not been considered. The present authors are not aware of quantitative computations involving preferential collision of differing particle sizes in the presence of a repulsive force. It is the purpose of this paper to examine the theory as it relates to preferential and limited aggregation (or coalescence). As will be seen, some of the theoretical conclusions consistently describe many of the findings of investigators in the field.

THEORY

Rate of Preferential Aggregation or Coalescence— Let us assume that there are equal concentrations of spherical particles of three sizes, that is, spheres S_1, S_2, and S_3 of radii a_1, a_2, and a_3, respectively, where $a_1 < a_2 < a_3$. The dispersion is in an electrolyte solution and the particles are allowed to aggregate (coalesce) at 25°. The following question is asked: what are the probabilities of S_1 colliding with S_1, S_2, or S_3, of S_2 with S_2 or S_3, and of S_3 with S_3? By means of theory let us determine the initial rates of aggregation or coalescence for the various size pairs.

It will be assumed following the Derjaguin-Verwey-Overbeek concepts, the interparticle interaction results from electrical repulsion and the London-van der Waals attraction. According to the theories of Smoluchowski and Fuchs (7), the rate of collision between spherical particles of sizes i and j is given by:

$$G_{ij} = \frac{4\pi D_{ij} R_{ij} N_i N_j}{W_{ij}} \quad \text{(Eq. 1)}$$

where G is the initial rate, D is the Stokes-Einstein diffusion coefficient, R is the distance between centers of the spheres, N is the concentration of

particles, and W is the stability factor, which will be later discussed in detail. We may also write:

$$D_{ij} R_{ij} = \frac{kT}{6\pi\mu} \left(\frac{1}{a_i} + \frac{1}{a_j} \right) (a_i + a_j) \quad \text{(Eq. 2)}$$

where k is the Boltzman constant, T is the absolute temperature, and μ is the viscosity of the suspending medium. Then the initial rate is:

$$G_{ij} = \frac{2kT}{3\mu W_{ij}} \left(\frac{1}{a_i} + \frac{1}{a_j} \right) (a_i + a_j) N_i N_j \quad \text{(Eq. 3)}$$

The factor W_{ij} accounts for the energy barrier to aggregation and is given by:

$$W_{ij} = 2 \int_2^\infty \exp \left(\frac{V_{T(i,j)}}{kT} \right) \frac{ds}{s^2} \quad \text{(Eq. 4)}$$

where $s = R/\bar{a}$ and $\bar{a} = (a_i + a_j)/2$. The W_{ij} usually ranges from $1 \lesssim W < \infty$ and takes into account the double-layer potential, the concentration of electrolytes, London-van der Waal dispersion forces, and the particle sizes of the two spheres.

Potential Energy of Interaction— In Eq. 4 the $V_{T(i,j)}$ is the total potential energy of interaction between two particles and is given by the sum of the repulsive energy, $V_{R(i,j)}$, and the attraction energy, $V_{A(i,j)}$; thus:

$$V_{T(i,j)} = V_{R(i,j)} + V_{A(i,j)} \quad \text{(Eq. 5)}$$

The repulsive energy between interacting spheres of sizes i and j can be calculated by the approximate expression derived by Hogg, Healy, and Fuerstenau (8):

$$V_{R(i,j)} = \frac{\epsilon a_i a_j \psi_0^2}{(a_i + a_j)} \ln [1 + \exp. (-KH)] \quad \text{(Eq. 6)}$$

where ϵ is the dielectric constant of the medium, ψ_0 is the surface potential, K is the reciprocal of the Debye-Hückel thickness of the double layer, and H is the shortest distance between the surfaces of the spheres. The equation is valid for Ka_i and $Ka_j \gg 1$.

The attraction energy of particles is more difficult to determine because the force between particles is considerably reduced by the retardation between atoms. Since the retardation effect is a function of distance, a single expression for the attraction energy is not available. When a_i, $a_j \gg H$ and $H \lesssim 150°$ A, the attraction interaction energy can be calculated by the expression:

$$V_{A(i,j)} = -\frac{A a_i a_j}{6(a_i + a_j)H} \left(\frac{\lambda}{\lambda + 11.116H} \right) \quad \text{(Eq. 7)}$$

where A is the Hamaker constant, and λ is the characteristic wavelength of the atoms.

For $H \gtrsim 150°$ A,

$$V_{A(i,j)} = \frac{A a_i a_j}{(a_i + a_j)} \left[\frac{-2.45\lambda}{60\pi H^2} + \frac{2.17\lambda^2}{360\pi^2 H^3} - \frac{0.59\lambda^3}{1680\pi^3 H^4} \right] \quad \text{(Eq. 8)}$$

One should refer to the *Appendix* for the discussion of the retardation factor and the derivation of Eqs. 7 and 8.

CALCULATIONS

Computations employing Eqs. 3–8 were carried out for a wide range of conditions with the aid of the IBM 7090 digital computer. ψ_0 values from 0 to
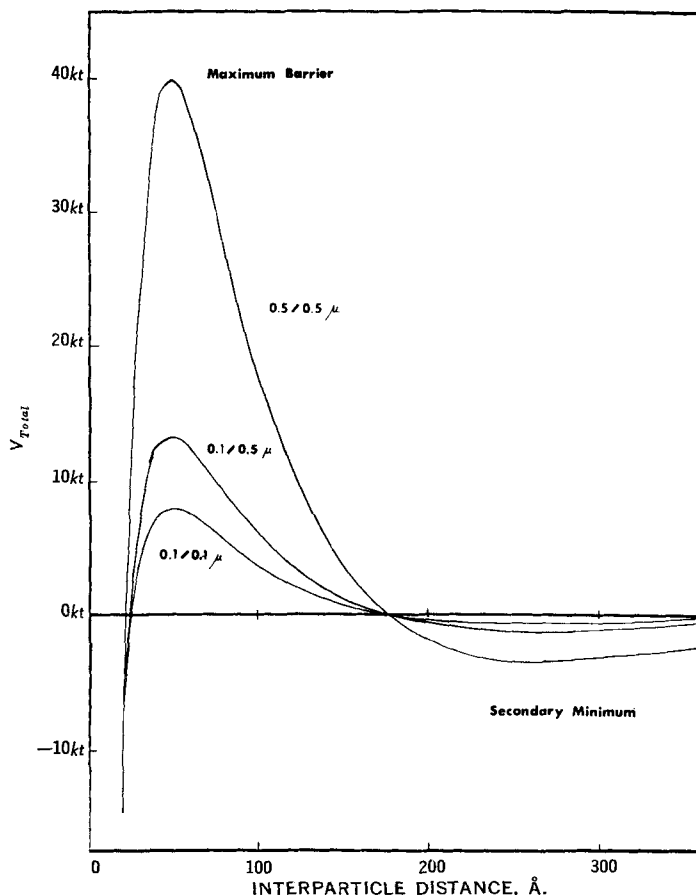
Fig. 1—Influence of particle sizes on the total potential energy of interaction. $A = 5 \times 10^{-13}$ erg, $\psi_0 = 25$ mv., and $K = 2 \times 10^6$ cm.$^{-1}$.

100 mv. and various radius combinations were taken at different K. Because the Hamaker constant is estimated (9, 10) to be somewhere in the neighborhood of 1 to 5×10^{-13} erg for most organic substances in water, calculations were made using the two values, 1×10^{-13} and 5×10^{-13}. The characteristic wavelength, λ, was taken to be 10^{-5} cm. Some plots of V_T versus H are shown in Figs. 1–3.

Table I presents some of the significant results. Calculated values of $V_{T\text{max}}$, the maximum in the V_T versus H curves, are shown. The rate constant, G', is defined as:

$$G' = \frac{G_{ij}}{N_i N_j} \qquad \text{(Eq. 9)}$$

DISCUSSION

Where K is large, *i.e.*, $K \gtrsim 0.4$ to 2×10^7, or when $\psi_0 \simeq 0$, it is seen (Table I) that, for essentially all particle sizes in the range of 0.1 to 5.0 μ radius, the rates of aggregation approach the Smoluchowski rates. Thus, in 1% NaCl solutions, maximum rates may be expected. Figure 4 shows the maximum limiting rate constants under these conditions for which W_{ij} equals unity.[1] The well-known preferential aggregation relationship due to Muller

(11) can be seen here. However, under such "rapid" aggregation conditions, the rate constant for a 0.1 μ–1.0 μ pair is only about three times greater than that for particles of the same size.

Let us now direct our attention to the region of kinetic stability where the rates may be regarded as neither very rapid nor very slow. In this intermediate stability region we note a dramatic change in importance of particle size. This can be seen in Table I and in Fig. 5. In Fig. 5 it can be seen how electrolyte concentration may markedly increase the preference for the aggregation (or coalescence) of small particles with each other or with large particles. Thus, when $K \simeq 2$ to 4×10^6 for $\psi_0 \simeq 25$ mv., it can be seen (Table I or Fig. 5) that the rate of aggregation (or coalescence) of 0.1-μ particles with itself or larger particles may be 10 to 30 orders of magnitude greater than that for two 0.5-μ particles. Comparing Fig. 5 with Fig. 6, we note that the rates for various particle sizes are highly sensitive to the Hamaker constant taken as 1×10^{-13} and 5×10^{-13} erg.

The above conclusions depend upon the assumption that other contributions to particle–particle repulsion are absent. Therefore, in the case of emulsion coalescence, strongly adsorbed barrier-forming interfacial films are assumed to be absent. In practice one would expect that when surface coverage of ionic emulsifiers is low, say about 5 to 10% of maximum coverage, the repulsion between two oil droplets in an aqueous medium would be

[1] Actually the limiting W_{ij} values may be somewhat less than unity when all repulsive barriers are removed because V_T will be negative (see Eq. 4).
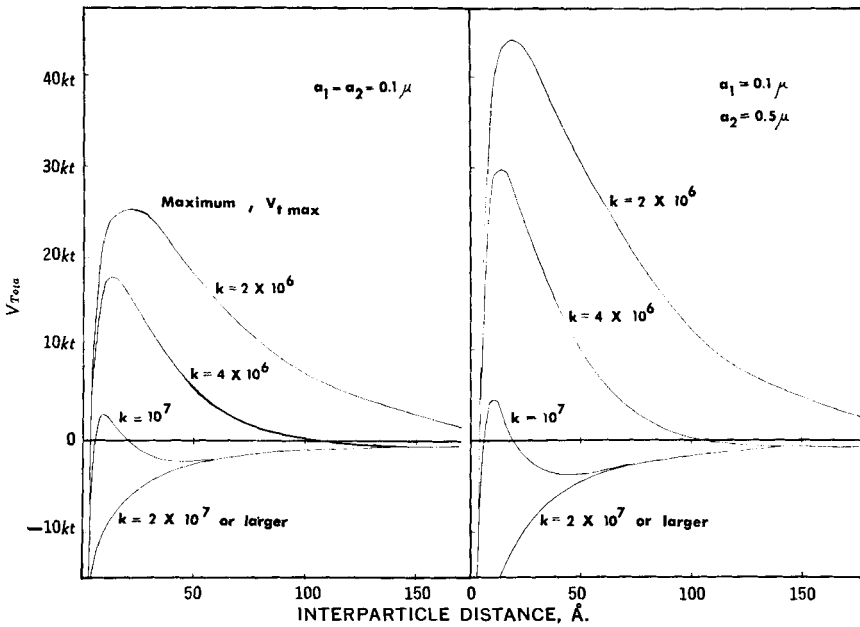
Fig. 2—Influence of electrolyte concentration on the total potential energy of interaction for two particle sizes. A $= 1 \times 10^{-13}$ *erg and* $\psi_0 = 25$ *mv.*
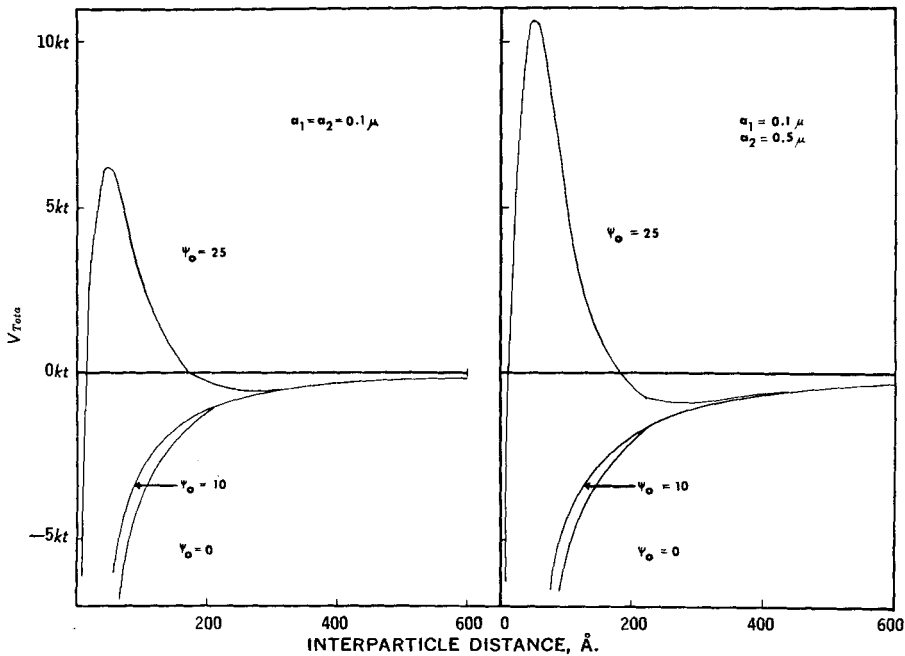

Fig. 3—Influence of surface potential on the total potential energy of interaction for two particle sizes. A $= 5 \times 10^{-13}$ *erg,* $\psi_0 = 25$ *mv., and* K $= 2 \times 10^6$ *cm.*$^{-1}$.

primarily electrical. These findings are consistent with the observations (3) that there is frequently an initial period of rapid coalescence with freshly prepared emulsions. Usually this is explained on the basis of the lack of sufficient stabilizer to provide a complete monolayer for the droplets. However, this explanation alone does not account for the relatively narrow size distributions that often result. The absence of small particles indicates that they preferentially disappear rapidly.

It is proposed that in a freshly prepared emulsion the shortage of surfactant prevents the formation of complete interfacial adsorbed films. Consequently, the rupture or displacement of the adsorbed molecules may not be rate determining in coalescence. Then if ψ_0 is low ($\gtrsim 25$ mv.) or if K is large, the rapid and selective disappearance of small droplets through coalescence would occur. The surviving larger droplets coalesce at a much slower rate as W_{ij} is extremely sensitive to particle size. Thus, a relatively narrow distribution would result if Brownian motion alone is inducing the coalescence.

TABLE I—SUMMARY OF DATA ON THE INFLUENCE OF ELECTROLYTE CONCENTRATION (K), SURFACE POTENTIAL (ψ_0), AND THE HAMAKER CONSTANT (A) ON THE MAXIMUM POTENTIAL INTERACTION ENERGY OF THE BARRIER ($V_{Tmax.}$) AND THE RATE CONSTANT FOR AGGREGATION (G')

ψ_0, mv.	K, cm.⁻¹	Radii 0.1 and 0.1 μ G'	$V_{Tmax./kT}^a$	Radii 0.1 and 0.5 μ G'	$V_{Tmax./kT}^a$	Radii 0.1 and 1.0 μ G'	$V_{Tmax./kT}^a$	Radii 0.5 and 0.5 μ G'	$V_{Tmax./kT}^a$
					A erg, 1 × 10⁻¹³				
0		11.2×10^{-12}	~0	20.2×10^{-12}	~0	33.9×10^{-12}	~0	11.2×10^{-12}	~0
10	2×10^6	5.2×10^{-12}	0.77	5.6×10^{-12}	1.28	8.4×10^{-12}	1.40	2.4×10^{-13}	3.84
	$>4 \times 10^6$	11.2×10^{-12}	~0	20.2×10^{-12}	~0	33.9×10^{-12}	~0	11.2×10^{-65}	~0
25	$>2 \times 10^7$	3.0×10^{-24}	25.73	5.8×10^{-28}	42.88	3.6×10^{-29}	46.78	1.1×10^{-66}	129.63
	4×10^6	2.4×10^{-17}	17.43	1.2×10^{-21}	29.05		31.69	6.3×10^{-47}	87.15
	1×10^7	8.6×10^{-13}	2.56	2.8×10^{-13}	4.26	3.1×10^{-13}	4.65	3.1×10^{-18}	12.79
	$>2 \times 10^7$	11.2×10^{-12}	~0	20.2×10^{-12}	~0	33.9×10^{-12}	~0	11.2×10^{-12}	~0
					A erg, 5 × 10⁻¹³				
0	$>2 \times 10^6$	11.2×10^{-12}	~0	20.2×10^{-12}	~0	33.9×10^{-12}	~0	11.2×10^{-12}	~0
10	$>2 \times 10^6$	11.2×10^{-12}	~0	20.2×10^{-12}	~0	33.9×10^{-12}	~0	11.2×10^{-12}	~0
25	$>4 \times 10^6$	19.4×10^{-14}	7.75	6.0×10^{-16}	12.91	5.7×10^{-16}	14.08	3.4×10^{-26}	38.73
		11.2×10^{-12}	~0	20.2×10^{-12}	~0	33.9×10^{-12}	~0	11.2×10^{-12}	~0

a Note that when $V_{Tmax./kT} < 0$, little repulsive barrier exists, hence aggregation is dependent on London-van der Waal attraction.
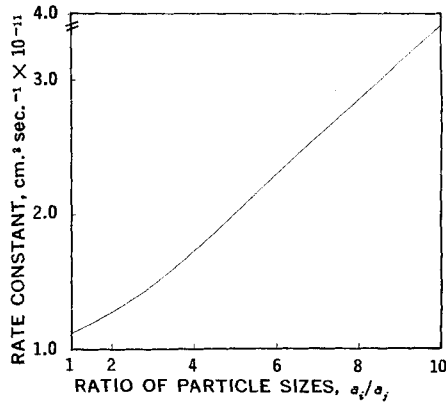

Fig. 4—Probability of rapid aggregation between particles of different sizes when the stability factor W_{ij} equals unity.

Gillespie (5) has discussed limited coalescence of oil-in-water emulsions stabilized by finely divided solids. He proposed a theory based on the rate of accretion of the solid stabilizer by the oil droplets. Furthermore, he found that there was an optimum concentration range for an ionic surfactant additive that produced the most uniform stable drops. This concentration range of the ionic surfactant appeared to produce a moderate or small electrical repulsive barrier. These findings are consistent with the theoretical results.

While the findings are only tentative, the precipitation of denatured proteins (2) near the isoelectric point appears to involve the formation of relatively uniform primary particles of around 1 μ diameter. Such narrow distributions are consistent with the above theory that selective aggregation of small particles with large ones take place. The extreme situation where only single denatured protein molecules deposit upon the larger particles would lead to the formation of relatively compact spherical particles of relatively narrow size ranges.

The authors believe that the results presented provide a much better understanding of the role of particle size in the mechanisms of aggregation and coalescence. It provides a possible scientific basis for tailor-making dispersion formulations of controlled size and size distributions.

APPENDIX

Attractive Energy between Unequal Spheres and the Effect of Retardation—Hamaker (12) was the first to describe the potential energy of attraction between unequal spheres, $V_{A(S_1/S_2)}$, of similar constitution. For $a_1, a_2 \gg H$, the limiting expression is:

$$V_{A(S_1/S_2)} = -\frac{A a_1 a_2}{6(a_1 + a_2)H} \quad \text{(Eq. 1a)}$$

where Hamaker's constant $A = \pi^2 q^2 \beta$, and q is the number of atoms per cm.³, β is the London constant, a_1, a_2, and H are defined as before.

Schenkel and Kitchener (10) made a thorough analysis of the retardation effect. Using the equations for $f(p)$ as a check that are presented in several references (10, 13), they derived empirical expressions that gave the best fit and that would give an analytic solution for interaction energies with modifications for the retardation effect. Accordingly,
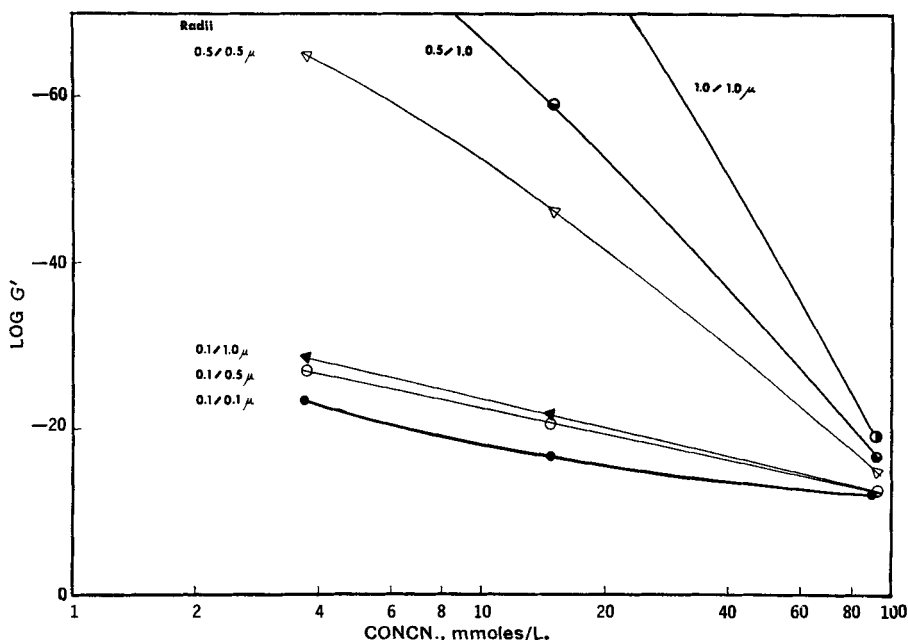
Fig. 5—Rate constant (G') *as a function of concentration of 1-1 electrolyte for various particle sizes.* A = 1×10^{-13} *erg and* ψ_0 = *25 mv.*
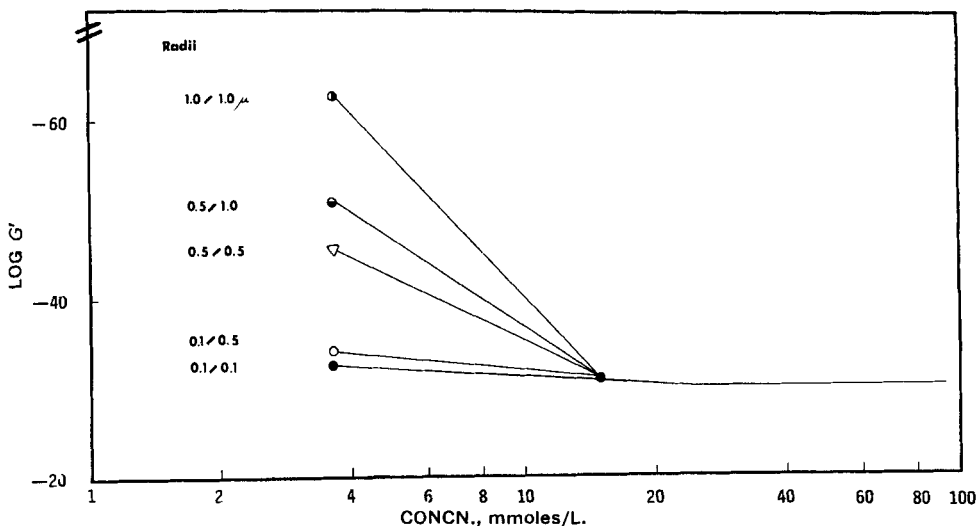

Fig. 6—Rate constant (G') *as a function of concentration of 1-1 electrolyte for various particle sizes.* A = 5×10^{-13} *erg and* ψ_0 = *25 mv.*

for the range of $0.5 < p < \infty$,

$$f(p) \sim \frac{2.45}{p} - \frac{2.17}{p^2} + \frac{0.59}{p^3} \quad \text{(Eq. 2a)}$$

For comparatively large distances, Casimir and Polder (14) showed that the London energy between atoms decays very rapidly due to retardation effects. Consequently, the London interaction energy of a pair of atoms of r distance apart,

$$V_{A(\text{London})} = -\frac{\beta}{r^6} \quad \text{(Eq. 3a)}$$

must be corrected so that

$$V'_{A(\text{at./at.})} = V_{A(\text{London})} f(p) \quad \text{(Eq. 4a)}$$

where $p = 2\pi r/\lambda$, and λ is the characteristic wave-

length of the atoms and β is the London constant. Equation 4a may be rewritten:

$$V'_{A(\text{at./at.})} =$$
$$- \frac{2.45\lambda\beta}{2\pi r^7} + \frac{2.17\lambda^2\beta}{(2\pi)^2 r^8} - \frac{0.59\lambda^3\beta}{(2\pi)^3 r^9} \quad \text{(Eq. 5a)}$$

In deriving the expressions for the retarded interaction energies for equal spheres, Schenkel and Kitchener used Derjaguin's method (15, 16) for calculating the interaction of spheres. It was pointed out that the algebra was simpler than for Hamaker's method (12) and that the results obtained were the same by both methods, provided it is only the limiting expressions that are required. In a similar manner, the method is applied to the interaction between unequal spheres.
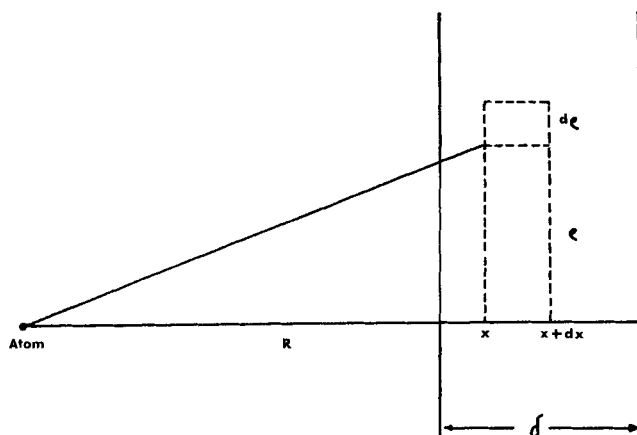
Fig. 7—*Geometry of the London-van der Waal interaction between an atom and an infinitely large plate of thickness δ. The plate is built up of infinitesimal rings of diameter ρ, cross-section dρdx at a distance (R + x) from the atom (17).*

Applying Eq. 4a to the geometry in Fig. 7, the interaction energy between an atom and all of the atoms in an infinitely large flat plate, $V'_{A(\text{at.}/p)}$, may be described by the superposition of their retarded attractive energies, i.e.,

$$V'_{A(\text{at.}/p)} = V''_A + V'''_A + V''''_A \quad \text{(Eq. 6a)}$$

where

$$V''_A = -\int_0^\delta \int_0^\infty \frac{2\pi q \phi \rho \, d\rho \, dx}{[(R+x)^2 + \rho^2]^{7/2}} \quad \text{(Eq. 7a)}$$

$$V'''_A = \int_0^\delta \int_0^\infty \frac{2\pi q \theta \rho \, d\rho \, dx}{[(R+x)^2 + \rho^2]^4} \quad \text{(Eq. 8a)}$$

$$V''''_A = -\int_0^\delta \int_0^\infty \frac{2\pi q Z \rho \, d\rho \, dx}{[(R+x)^2 + \rho^2]^{9/2}} \quad \text{(Eq. 9a)}$$

and $\phi = 2.45\lambda\beta/2\pi$; $\theta = 2.17\lambda^2\beta/(2\pi)^2$; and $Z = 0.59\lambda^3\beta/(2\pi)^3$. Also, the Hamaker constant $A = \pi^2 q^2 \beta$. It follows that the interaction between two flat plates, $V'_{A(p/p)}$, is

$$V'_{A(p/p)} = \int_R^\infty q V'_{A(\text{at.}/p)} dR \quad \text{(Eq. 10a)}$$

If the surface of two spheres is thought to be built up of parallel pairs of infinitesimally small rings with radius h (8), the interaction of unequal spheres, $V'_{A(S_1/S_2)}$, is expressed by:

$$V'_{A(S_1/S_2)} = 2\pi\left(\frac{a_1 a_2}{a_1 + a_2}\right) \int_H^\infty V'_{A(p/p)} dH$$

$$\text{(Eq. 11a)}$$

The edge effects are neglected. Finally, the limiting expression for the interaction energy for unequal spheres is:

$$V'_{A(S_1/S_2)} = \frac{A a_1 a_2}{a_1 + a_2}\left[-\frac{2.45\lambda}{60\pi H^2} + \frac{2.17\lambda^2}{360\pi^2 H^3} - \frac{0.59\lambda^3}{1680\pi^3 H^4}\right]$$

$$\text{(Eq. 12a)}$$

(for $H \ll a_1, a_2$; $0.5 < p_0 < \infty$).

Since $p_0 = 2\pi H/\lambda$ and λ is usually taken as 10^{-5} cm., Eq. 12a should not be used for approximately $H < 150°\ A$. It is noteworthy that the equation reduces to the identical expression[2] obtained by

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[2] See equation (x) in the appendix of *Reference 10*.

Schenkel and Kitchener for interaction of equal spheres, i.e., $a_1 = a_2$.

For the range below $p_0 = 0.5$, the retardation effect is still significant until the interparticle distance is comparatively very small, in which case Eq. 1a will apply. Based on extrapolation of the attractive potential energy curve, an empirical expression that represents the region $0 < p_0 < 2$, approximately $H < 300°\ A$, is given by Eq. 7.

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🔑 *Keyphrases*

Heterodispersed systems

Coalescence, aggregation—small particles

Electrical barrier, effect—coalescence, aggregation

Energy of interaction potential—small particles

Spheres, unequal—attractive energy, retardation