# VI. THE INTERACTION BETWEEN COLLOIDAL PARTICLES [1]

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## § 1.   INTRODUCTION

It has already been shown in chapter II that the stability of hydrophobic colloids is largely governed by the interaction of their particles. If a repulsion of sufficient strength exists between the particles, a sol is stable; if this repulsion is absent or even reverted into an attraction, the stability is lost and the system coagulates.

The interaction of colloidal particles is supposed to contain two components. One, the repulsive factor finds its origin in the electrochemical double layer. The other component is the general LONDON-VAN DER WAALS attraction.

The stability of colloids is not a question of quality to be answered simply by "yes" or "no", but a question of quantity. A measure of the stability is found in the velocity of coagulation, which may vary from very quick (flocculation within a few seconds) to immeasurably slow. Consequently for a complete discussion of the stability the kinetics of coagulation have to be taken into account.

In this chapter VI the interaction between colloidal particles will be treated mainly from a theoretical point of view.

The kinetics of flocculation are discussed in chapter VII. Chapter VIII gives the synthesis of these two fields resulting in a theory of the stability of colloids [2]. This theory is compared with experiments. Moreover, as far as experimental data on stability exist which are not yet related to the theory, they will also be treated in chapter VIII.

## § 2.   FREE ENERGY OF A SYSTEM OF ELECTROCHEMICAL DOUBLE LAYERS

A problem of interaction can be treated by considering either the energy of interaction or the force derived from this energy. In our case the treatment of the energy is to be preferred, among other things, because the interaction has to be compared to the *energy* of the BROWNian motion. The force of interaction can always be found easily by differentiation of the energy with respect to the distance. Because the double layer is a system in thermal equilibrium we are mainly concerned with its *free* energy (or free enthalpy, which is practically the same in condensed systems), not with its total energy, as the free energy gives a measure of the work that can be performed.

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In chapter IV the free energy of the double layer has been treated extensively. Two extreme cases have been considered there, one, the electrocapillary case (chapter IV, § 3a, p. 119) where the double layer was formed by an external current and the other (chapter IV, § 3b, p. 122), the reversible one, in which the double layer was formed by adsorption of ions (or electrons in the case of redox-equilibria) from the solution.

Evidently in colloidal systems the possibility of charging by an external current is absent [1] and only the second method remains.

By straightforward thermodynamic reasoning it has been proved in chapter IV (eq. (29) p. 123, eq. (70, 71) p. 140) that the free energy of the double layer, or of a system of double layers, is equal to

$$G_{\text{double layer}} = - \int_0^{\psi_o} Q \, d\psi \tag{1}$$

where $\psi$ is the potential difference between the two phases, assuming arbitrarily that this potential difference is zero at the zero point of charge. $Q$ is the charge of the surface. $\psi_0$ is the double layer potential after equilibrium has been established.

The significance of eq. (1) might seem doubtful to the reader who remembers that the potential difference between two phases is not accessible to experimental determination. It should, however, be pointed out that *changes* in this potential difference can be determined experimentally and, given our definition of the zero point of $\psi_o$, $\psi_o$ is in fact only a change in the potential difference between two phases. For a more detailed discussion of this question the reader is referred to chapter IV § 3, p. 118.

A second formulation for the free energy of the double layer has been derived in chapter IV, § 4f, p. 139. This formulation is based on the imaginary charging process used in the DEBYE and HÜCKEL theory of strong electrolytes, in which the charge of all the ions (and electrons) in the system is gradually increased from zero to their normal value. If the stage of the charging process is indicated by $\lambda$, $\lambda e_i$ being the momentary charge of an ion with normal charge $e_i$, $\lambda$ increases from 0 to 1. According to eq. (76) of chapter IV p. 142 the free energy of the double layer is then given by

$$G_{\text{double layer}} = G(0) + \int_0^1 \frac{d\lambda}{\lambda} \int \rho' \, \psi' \, dV \tag{2}$$

the integration being carried out over the whole solution phase at constant surface potential $\psi_o$. In eq. (2) $\rho'$ denotes the charge density, $\psi'$ the potential at stage $\lambda$ and $dV$ a volume element in the solution. The potential $\psi'$ is considered to be zero far away from all the interfaces.

$G(0)$ is zero for a flat double layer or for two parallel flat double layers, but it has a finite value in the case of curved surfaces.

Although physically the two equations (1) and (2) are completely equivalent [2], in some cases eq. (1) and in other cases eq. (2) is more suitable in mathematical respects and we shall always apply that equation which leads most easily to the purpose.

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[1] Even if an external current could be used in the preparation of the sol, the unavoidable leakage would cause these charges to disappear very soon after the formation.

[2] H. B. G. CASIMIR, in E. J. W. VERWEY and J. TH. G. OVERBEEK, *Theory of the stability of hydrophobic colloids*, Amsterdam 1948 pp. 60, 63; S. LEVINE, *Phil. Mag.*, (7) 41 (1950) 53.

The equilibrium value of the surface potential $\psi_\circ$ is completely determined by the composition of the two phases. More specifically, it is linearly dependent upon the difference in chemical potential $\mu_i$ of the potential determining ions in the two phases. Consequently (*cf.* chapter IV, § 3d, p. 124, § 6, p. 159).

$$z_i \, e \, \mathrm{d} \psi_\circ = \mathrm{d} \Delta \, \mu_i \tag{3}$$

or

$$\psi_\circ = \text{const.} + \frac{\Delta \, \mu_i}{z_i \, e} \tag{4}$$

The constant in eq. (4) which is simply related to the chemical potential at the zero point of charge, is not dependent upon the geometrical configuration of the system. Consequently $\psi_\circ$ is also independent upon configuration, and the interaction of double layers, involving changes in configuration (distance) should be studied at a constant value of $\psi_\circ$ as far as equilibrium situations are involved and provided the bulk concentration of the ions $i$ does not change materially during interaction.

It may be, however, that during a rapid interaction, like that occurring during a BROWNian encounter of two sol particles, thermodynamic equilibrium is not maintained. In that case it is impossible to deduce the free energy of interaction from equation (1) or (2). Perhaps the most obvious form of disequilibrium is a complete lack of exchange of ions (or electrons) between the two phases, which means that the surface *charge* remains constant in contradistinction to the equilibrium case, where the surface *potential* remains constant. Then the contribution to the free energy of the transition of ions from one phase to the other need not be considered. The important part of the free energy is then the work necessary to charge the surface in a reversible way starting from zero charge. The charge of the potential determing ions is imagined to be transported gradually from the solution to the surface. After each small increase of the surface charge the charges in the solution are allowed to rearrange themselves according to a new equilibrium. In this rearrangement in the solution no work is lost or gained and the electrical part of the free energy of the double layer can be written

$$G_{\text{electr.}} = \int_0^Q \psi_\circ' \, \mathrm{d}Q' \tag{5}$$

where $\psi_\circ'$ is the momentary surface potential and $Q'$ the surface charge with $Q$ as its final value.

In some cases of interaction eq. (5) might be a better approximation than eq. (1) or (2), although we shall more often base our treatment on the equilibrium case.

## § 3.  THE INTERACTION OF TWO PARALLEL PLANE DIFFUSE DOUBLE LAYERS

### a.  The distribution of charge and potential between two parallel flat plates

The distribution of charge and potential in one double layer has been treated in chapter IV. We shall now extend this treatment to the case of two parallel double layers which have approached each other until the diffuse parts of the two double layers overlap each other to a measurable extent. This is the case when the distance between the two surfaces is of the same order as the extension of the double layer, $1/\varkappa$ [1].

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[1] The symbols used in this chapter have the same meaning as in chapter IV except when the contrary is specifically stated.

When two parallel surfaces, each bearing a double layer of the same sign, approach each other to a distance where the two diffuse double layers begin to interfere, neither of them can develop completely. As a consequence the potential between the two surfaces nowhere reaches the level it has at a large distance from the surface. This last-mentioned level will, as has been done in chapter IV, be chosen as the zero of potential.
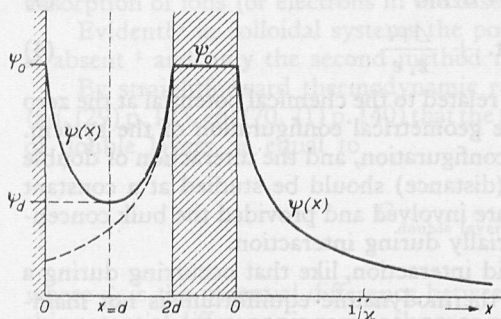


Fig. 1.   Schematic representation of the electric potential between two plates, in comparison with that for a single double layer.

On the surfaces the potential retains the same value it has for a free surface because this potential is completely determined by the thermodynamic equilibrium as expressed by eq. (4).

A simple consideration of the symmetry of the case shows that the minimum value of the potential must be reached just halfway between the two surfaces. Fig. 1 shows schematically the course of this potential.

In this and the following chapters, we shall often be forced to restrict our considerations to double layers of the GOUY-CHAPMAN type, neglecting the STERN correction [1]. Calculations on the interaction of STERN-GOUY layers are still scarce and incomplete, and further developments in this direction will have to be awaited before they can succesfully be applied to the problem of the stability of hydrophobic colloids. Fortunately, many salient points can be treated from the point of view of simple diffuse double layers and in more complicated cases it is often possible to take account of the influence of the STERN-layer in a qualitative or semi-quantitative way.

For double layers of the GOUY-CHAPMAN type the course of the potential between the two surfaces can again be described by the combination of the POISSON and the BOLTZMANN equations (cf. chapter IV, § 4a, p. 126). The only difference from the case of a single double layer is found in the boundary conditions. There the boundary conditions were that the potential and its derivatives are all zero far away from the surface, and in the case of interaction we only know that halfway between the plates the potential has a minimum value so that its first derivative is zero.

The equation to be solved is:

$$\Delta \psi = \frac{d^2 \psi}{dx^2} = \frac{4 \pi e}{\varepsilon} \left( n_- z_- e^{\frac{z_- e \psi}{kT}} - n_+ z_+ e^{-\frac{z_+ e \psi}{kT}} \right) \tag{6}$$

subject to the boundary conditions

$$\psi = \psi_0 \text{ for } x = 0$$
$$\psi = \psi_d \text{ for } x = d \tag{7}$$
$$\frac{d\psi}{dx} = 0 \text{ for } x = d.$$

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[1] Cf. Chapter IV, § 4. p. 126.

The coordinate $x$ is measured from one of the plates. The distance between the plates is equal to $2\,d$. The other symbols have the same meaning as in chapter IV (p. 115). The first integration of (6) leads to [1]

$$\frac{d\psi}{dx} = -\sqrt{\frac{8\pi kT}{\varepsilon}} \sqrt{n_- e^{\frac{z_- e\psi}{kT}} + n_+ e^{\frac{-z_+ e\psi}{kT}} - n_- e^{\frac{z_- e\psi_d}{kT}} - n_+ e^{\frac{-z_+ e\psi_d}{kT}}} \tag{8}$$

It would be possible to carry out the second integration of (8) numerically or graphically, but owing to the great number of essential variables, (valency type and concentration of electrolytes, surface potential, distance between the plates) this would lead to a tremendous amount of work before any useful survey of the important cases could be obtained. Therefore some simplifications are introduced.

In the first place eq. (8) can be integrated when the potential is small everywhere. Eq. (8) then reduces to

$$\frac{d\psi}{dx} = -\varkappa\sqrt{\psi^2 - \psi^2_d} \tag{9}$$

where $\varkappa = \sqrt{\dfrac{4\pi e^2 (n_+ z^2_+ + n_- z_-^2)}{\varepsilon kT}}$

and the integration leads to

$$\psi = \psi_\circ \frac{\cosh \varkappa\,(d-x)}{\cosh \varkappa\,d} \text{ and } \psi_d = \psi_\circ \frac{1}{\cosh \varkappa d} \tag{10}$$

Although these expressions are useful in certain cases, they are of little help in the understanding of colloid stability.

The most outstanding feature of the stability of hydrophobic sols is the great influence of the valency of electrolytes, especially the counterions, as expressed by the rule of SCHULZE and HARDY (cf. chapter II, § 5 c. 1, p. 81). Now in eq. (9) and (10) the valency of the electrolytes is completely expressed in the quantity $\varkappa$ and there the roles of the valency of positive and negative ions are perfectly symmetrical.

Consequently, in order to get an explanation of the flocculation values of sols on the basis of the diffuse double layer picture, the approximation of small potentials is of no use. Another simplification however is allowed. For high values of $\psi$, the value of eq. (8) is almost wholly determined by the positive powers of $e$, whereas the negative powers are so small that they are practically without influence. This is in accordance with the fact that the flocculation value of a sol is practically independent of the valency of the ions bearing the same sign as the colloidal particles. Thus no essential features are lost in restricting the discussion to the case of symmetrical electrolytes, which gives a considerable mathematical simplification. Calling the valency of this electrolyte $z$ and its concentration $n$, eq. (8) simplifies to

$$\frac{d\psi}{dx} = -\sqrt{\frac{8\pi n kT}{\varepsilon}} \sqrt{2 \cosh \frac{z e \psi}{kT} - 2 \cosh \frac{z e \psi_d}{kT}} \tag{8'}$$

Introducing now the variables

$$Y = \frac{z e \psi}{kT}, Z = \frac{z e \psi_\circ}{kT}, U = \frac{z e \psi_d}{kT}.$$

and $\xi = \varkappa x$.

[1] The negative sign has to be used for positive values of $\psi$ when $0 \leqslant x < d$.

we may write

$$\frac{dY}{d\xi} = - \sqrt{2 \cosh Y - 2 \cosh U} \qquad (11)$$

This differential equation, when integrated between the values $\xi = 0$ and $\xi = \varkappa d$, leads to a relation between the surface potential $(Z)$, the potential halfway between the plates $(U)$ and their distance $(\varkappa d)$. This relation can be expressed by means of elliptical integrals and is

$$\varkappa d = 2 e^{-\frac{U}{2}} \left[ F\left( e^{-U}, \frac{\pi}{2} \right) - F\left( e^{-U}, \text{ arc sin } e^{-\frac{Z-U}{2}} \right) \right] \qquad (12)$$

where $F(k, \varphi) = \displaystyle\int_0^{\varphi} \frac{d\alpha}{\sqrt{1 - k^2 \sin^2 \alpha}}$

is an extensively tabulated function [1]. Eq. (12) has been tabulated by VERWEY and OVERBEEK [2]. Their results are represented in Table 1 and Fig. 2.

For the further developments it is useful to consider the case of small interaction when the two surfaces are still relatively far apart. Then the potential between the two surfaces can be given in a good approximation by a simple summation of two independent and undisturbed double layers as is illustrated by Fig. 3.

In this case we may set

$$U = 2 Y'_d$$

in which $\psi'_d = \dfrac{kT \, Y'_d}{z \, e}$ is the potential of a single double layer at a distance $d$ from the surface. Now according to eq. (51) of chapter IV this $Y'_d$ is equal to
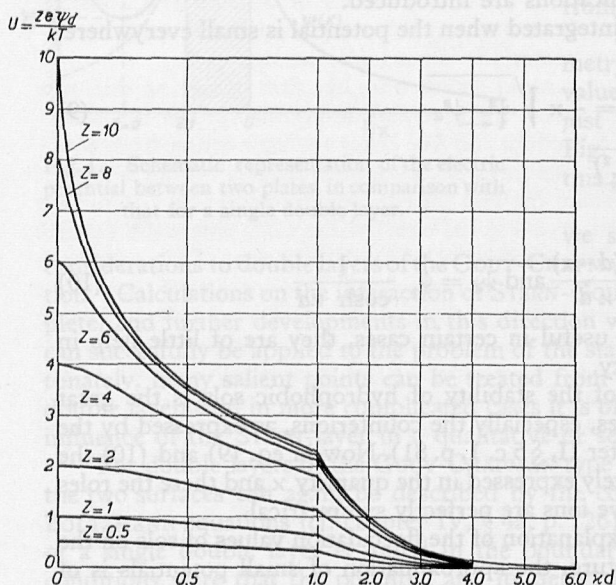


$U = \dfrac{ze\psi_d}{kT}$

Fig. 2. Potential $(\psi_d)$ half-way between the plates as a function of the plate distance $(2d)$ for different values of the surface potential $(\psi_0)$. In the figure the values of $U = \dfrac{ze \, \psi_d}{k \, T}$, $Z = \dfrac{ze \, \psi_0}{kT}$ and $\varkappa d$ are given.

$$Y'_d = 4 \gamma e^{-\varkappa d} \quad \text{in which } \gamma = \frac{e^{z/_2}-1}{e^{z/_2}+1}$$

and consequently for large values of $\varkappa d$ (and any value of $Z$)

$$U = 8 \gamma e^{-\varkappa d} \qquad (13)$$

[1] cf. E. JAHNKE and F. EMDE, Tables of functions, 4th ed., New York 1945, p. 52 et seq.
[2] E. J. W. VERWEY and J. TH. G. OVERBEEK, Theory of the stability of lyophobic colloids, Amsterdam 1948, p. 68.

TABLE 1

$\varkappa d$ AS A FUNCTION OF $Z$ AND $U$ ACCORDING TO EQ. (12)

$$Z = \frac{ze\psi_o}{kT} \qquad U = \frac{ze\psi_d}{kT}$$

| | Z-U=0.1 | Z-U=0.3 | Z-U=0.6 | U=9 | U=8 | 7 | 6 | 5 | 4 | 3 | 2 | 1 | 0.5 | 0.25 | 0.1 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Z = 10 | 0.00434 | 0.00836 | 0.01337 | 0.02042 | 0.04374 | 0.08128 | 0.1429 | 0.2444 | 0.4117 | 0.6879⁵ | 1.148 | 1.962 | 2.721 | 3.440 | 4.366 |
| 9 | 0.007324 | 0.01379 | 0.02208 | | 0.03367 | 0.07211 | 0.1340 | 0.2356 | 0.4030 | 0.6792 | 1.139 | 1.953 | 2.712 | 3.431 | 4.357 |
| 8 | 0.01208 | 0.02273 | 0.03642 | | | 0.05551 | 0.1189 | 0.2210 | 0.3885 | 0.6647⁵ | 1.124⁵ | 1.939 | 2.698 | 3.417 | 4.343 |
| 7 | 0.0199 | 0.03748 | 0.06005 | | | | 0.09154 | 0.1961 | 0.3644 | 0.6407 | 1.101 | 1.915 | 2.674 | 3.393 | 4.318 |
| 6 | 0.03275 | 0.06179 | 0.09900 | | | | | 0.1509 | 0.3232 | 0.6010 | 1.061 | 1.876 | 2.635 | 3.354 | 4.280 |
| 5 | 0.05410 | 0.10185 | 0.1632 | | | | | | 0.2488 | 0.5333 | 0.9955 | 1.811 | 2.570 | 3.290 | 4.215 |
| 4 | 0.08915 | 0.1680 | 0.2692 | | | | | | | 0.4105 | 0.8837 | 1.702 | 2.462 | 3.181 | 4.107 |
| 3 | 0.1471 | 0.2774 | 0.4455 | | | | | | | | 0.6813 | 1.518 | 2.280 | 2.998 | 3.924 |
| 2 | 0.2435 | 0.4643 | 0.7513 | | | | | | | | | 1.178 | 1.958 | 2.680 | 3.608 |
| 1 | 0.4353 | 0.8551 | 1.532 | | | | | | | | | | 1.279 | 2.035 | 2.971 |
| 0.5 | 0.8706 | 1.558 | | | | | | | | | | | | 1.309 | 2.241 |

$z \dfrac{e\psi}{kT}$
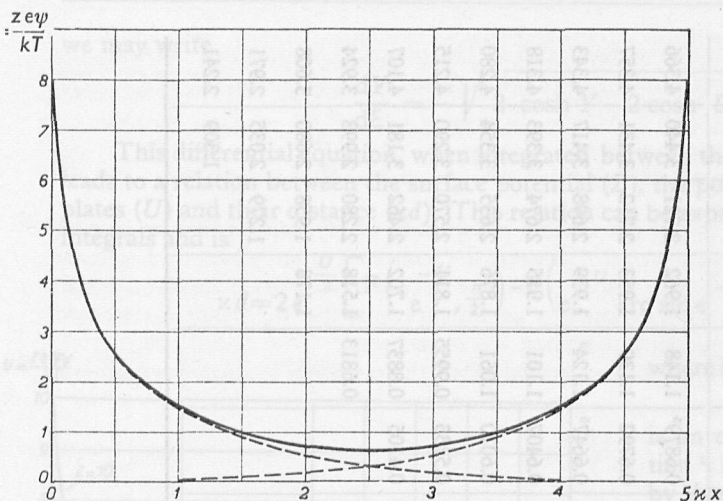


Fig. 3. Electric potential function between two plates ($Z = 8$) for small interaction ($\kappa d = 2.5$). Approximately, the potential can be built up additively from the electric potential functions of the two single double layers separately (dotted lines).

Inspecting now for a moment eq. (8) or eq. (11), one can see that the slope of the potential curve is the smaller, the larger the value of $\psi_d$ (or $U$). As the slope at the surface is directly proportional to the surface charge, this charge diminishes with increasing interaction and even goes to zero in the limiting case when the two surfaces come into contact. The same conclusion follows from the physical picture of the interaction of double layers. As a consequence of the neighbourhood of two double layers each of them separately cannot develop to its full extent, which is equivalent to saying that the total charge in the double layer is less than without interaction.

The mathematical expression for the double layer charge is quite simple.

$$\sigma = - \frac{\varepsilon}{4\pi}\left(\frac{d\psi}{dx}\right) x = 0 =$$

$$\sqrt{\frac{n\,\varepsilon\,kT}{2\pi}} \cdot \sqrt{2\cosh Z - 2\cosh U} \quad (14)$$

Fig. 4 shows the dependence of the surface charge on the separation distance of the two surfaces for a number of values of the surface potential. It is seen how, especially for large surface potentials, the charge changes only appreciably when the distance is small compared to $\dfrac{1}{\kappa}$.

### b. The free energy of two parallel double layers and the repulsion between the surfaces bearing them

Having now established the relations between charge, potential, and the distance between the two surfaces, it is possible by application of the equation
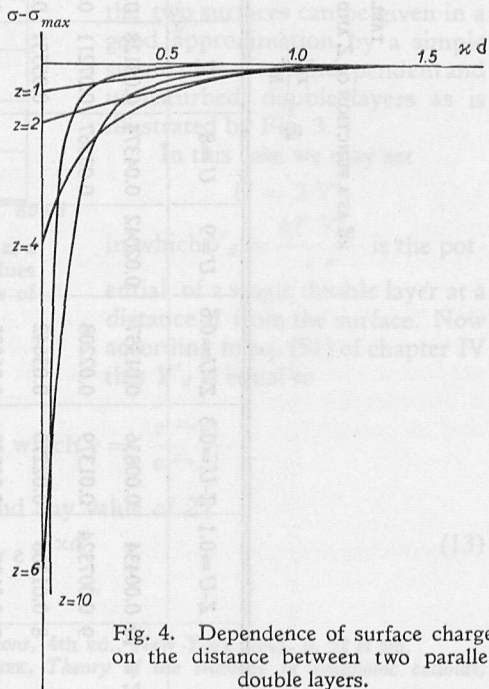
$\sigma - \sigma_{max}$



Fig. 4. Dependence of surface charge on the distance between two parallel double layers.

(1) or (2) (see p. 246), to determine the free energy of the double layer system [1]. Calling the free energy per cm² of each of the two plates 2 $G$, the integration of eq. (2) leads to

$$G = -\frac{2\,n\,kT}{\varkappa}\left[\frac{\varkappa d}{2}\left(3e^{U} - 2 - e^{-U}\right) + 2\sqrt{2\cosh Z - 2\cosh U} - \right.$$

$$\left. - 4e^{\frac{U}{2}}\left\{E\left(e^{-U},\frac{\pi}{2}\right) - E\left(e^{-U}, \arcsin e^{-\frac{Z-U}{2}}\right)\right\}\right]$$

(15)

$$\text{in which } E\,(k, \varphi) = \int_{0}^{\varphi}\sqrt{1 - k^2\sin^2\alpha}\; d\alpha$$

For $\varkappa\, d \longrightarrow \infty$ this expression is equivalent to the one found already in chapter IV eq. (73) p. 141 *viz*.

$$G_{d\longrightarrow\infty} = -\frac{2\,n\,kT}{\varkappa}\left(4\cosh\frac{Z}{2} - 4\right).$$

(16)

Now the stability of colloids is not determined by the value of the free energy itself but by the *change* in free energy when the two surfaces approach each other from an infinite distance of separation.

This change of the free energy is equal to the amount of work that has to be performed against the forces arising from the interaction of double layers.

Therefore we define the potential energy of repulsion (repulsive potential) $V_R$ per cm² cross section of the plates

$$V_R = 2\,(G - G_\infty)$$

(17)

As the reciprocal thickness of the double layer, $\varkappa$, is proportional to the valency $z$ and to the square root of the concentration, $\sqrt{n}$ of the electrolyte, both eqs. (15) and (16) can be expressed as $\dfrac{\varkappa}{z^2}$ times a function of $U$ and $Z$. By eq. (12) $\varkappa d$ is given as a function of $U$ and $Z$, and consequently if this function is known, $V_R$ can be calculated as a function of $\varkappa\, d$.

In Table 2 we give the values of f $(U, Z)$, this function being defined as

$$f\,(U, Z) = \frac{z^2}{\varkappa}\,V_R$$

(18)

whereas for convenience the corresponding values of $\varkappa d$ have also been given.

The function f $(U, Z)$ is proportional to the square of the absolute temperature and to the dielectric constant. Table 2 gives its values for water at 25° C, *viz*, for $\varepsilon = 78.55$ and $T = 298.1$. When the table has to be applied to another temperature $T_1$ and a dielectric constant $\varepsilon_1$ the values of f $(U, Z)$ have to be multiplied by $\varepsilon_1\,T_1^2\,/78.55\,(298.1)^2$.

Fig. 5 gives a graphic survey for part of the values of Table 2, especially for the cases of large potentials and strong interaction. In the small table in the figure the units of the ordinate have been indicated for a number of relevant values of $\varkappa$ and the valency.

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[1] We follow here the treatment given by VERWEY and OVERBEEK, *l.c.* Work by A. J. CORKILL and L. ROSENHEAD, *Proc. Roy. Soc. London*, A 172 (1939) 410 and older work by S. LEVINE and G. P. DUBE, *Trans. Faraday Soc.*, 36 (1940) 215, on the same subject are believed to be incorrect because the influence of entropy and of the chemical energy involved in the passing of ions from one phase to the other is not sufficiently taken into account.

TABLE 2

$f(U, Z) = (z^2/\varkappa) V_R$ in $10^{-7}$ dynes, and corresponding values of $\varkappa d$, for different values of $Z = ze\,\psi_o/kT$

($U = ze\,\psi_d/kT$; $V_R$ = repulsive potential due to the double layer interaction for two parallel plates per cm² plate surface).
The numbers given have been computed for a temperature of 25° C and a dielectric constant of 78.55.

| | | $U=Z$ | $U = Z—0.1$ | $U = Z—0.3$ | $U = Z—0.6$ | $U=9$ | $U=8$ | $U=7$ | $U=6$ | $U=5$ | $U=4$ | $U=3$ | $U=2$ | $U=1$ | $U=0.5$ | $U = 0.25$ | $U=0.1$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $Z=10$ | f (U, Z) | 268.3 | 228.2 | 192.6 | 160.0 | 127.1 | 75.4 | 44.1 | 25.4 | 14.1 | 7.36 | 3.42 | 1.26 | .26 | .06 | .015 | .0023 |
| | $\varkappa d$ | .0000 | .00434 | '00836 | .0134 | .0204 | .0437 | .0813 | .143 | .244 | .412 | .690 | 1.148 | 1 962 | 2.721 | 3.440 | 4.366 |
| $Z=9$ | f (U, Z) | 161.5 | 135.2 | 115.2 | 95.6 | | 76.3 | 44.3 | 25.4 | 14.1 | 7.36 | 3.42 | 1.26 | .26 | .06 | .015 | .0023 |
| | $\varkappa d$ | .0000 | .0073 | .0138 | .0221 | | .0337 | .0721 | .134 | .236 | .403 | .679 | 1.139 | 1.953 | 2.712 | 3.431 | 4.357 |
| $Z=8$ | f (U, Z) | 96.52 | 80.56 | 68.56 | 56.60 | | | 44.8 | 25.4 | 14.1 | 7.36 | 3.42 | 1.26 | .26 | .06 | .015 | .0023 |
| | $\varkappa d$ | .0000 | .0121 | .0227 | .0364 | | | .0555 | .119 | .221 | .388 | .665 | 1.124 | 1.939 | 2.698 | 3.417 | 4.343 |
| $Z=7$ | f (U, Z) | 57.13 | 47.46 | 40.18 | 32.89 | | | | 25.8 | 14.17 | 7.36 | 3.42 | 1.26 | .26 | .06 | .015 | .0023 |
| | $\varkappa d$ | .0000 | .0199 | .0375 | .0600 | | | | .0915 | .196 | .364 | .641 | 1.101 | 1.915 | 2.674 | 3.393 | 4.318 |
| $Z=6$ | f(U, Z) | 33.27 | 27.47 | 23.04 | 18.66 | | | | | 14.38 | 7.39 | 3.42 | 1.26 | .26 | .06 | .015 | .0023 |
| | $\varkappa d$ | .0000 | .0327 | .0618 | .0990 | | | | | .1509 | .323 | .601 | 1.061 | 1.876 | 2.635 | 3.354 | 4.280 |
| $Z=5$ | f (U, Z) | 18.83 | 15.32 | 12.69 | 10.07 | | | | | | 7.52 | 3.43 | 1.26 | .26 | .06 | .015 | .0023 |
| | $\varkappa d$ | .0000 | .0541 | .1018 | .1632 | | | | | | .2488 | .533 | .995 | 1.811 | 2.570 | 3.290 | 4.215 |
| $Z=4$ | f (U, Z) | 10.13 | 8.07 | 6.51 | 4.97 | | | | | | | 3.50 | 1.26 | .26 | .06 | .015 | .0023 |
| | $\varkappa d$ | .0000 | .0891 | .1680 | .2692 | | | | | | | .4105 | .884 | 1.702 | 2.462 | 3.181 | 4.107 |
| $Z=3$ | f (U, Z) | 4.962 | 3.793 | 2.913 | 2.061 | | | | | | | | 1.291 | .26 | .06 | .015 | .0023 |
| | $\varkappa d$ | .0000 | .1471 | .2774 | .4455 | | | | | | | | .681 | 1.518 | 2.280 | 2.998 | 3.924 |
| $Z=2$ | f (U, Z) | 1.993 | 1.413 | .966 | .584 | | | | | | | | | .265 | .06 | .015 | .0023 |
| | $\varkappa d$ | .0000 | .2435 | .4643 | .751 | | | | | | | | | 1.178 | 1.958 | 2.680 | 3.608 |
| $Z=1$ | f (U, Z) | .4682 | .271 | .135 | .0348 | | | | | | | | | | .063 | .015 | .0023 |
| | $\varkappa d$ | .0000 | .4356 | .855 | 1.532 | | | | | | | | | | 1.279 | 2.035 | 2.971 |

Before continuing the development of the theory the reader's attention is drawn to the absolute magnitude of this repulsive potential. For an electrolyte concentration of $1/1000$ normal, that is for $\varkappa = 10^6$ the repulsive potential for intermediate values of $\varkappa d$ is of the order of 1 erg/cm² which means that an interaction energy larger than $\cdot kT$ ($= 4 \cdot 10^{-14}$ ergs) is reached for a cross section larger than $(20 \text{ Å})^2$, proving that the energies corcerned may be expected to be significant for colloid stability.

### c. The force between two flat double layers and an approximate expression for the repulsive potential

LANGMUIR [1], DERJAGUIN [2] and BERGMANN, LÖW-BEER, and ZOCHER [3] have also considered the repulsive *force* between two double layers. Although these considerations add nothing essential to the developments of the preceding sub-paragraph, we reproduce here a simple derivation of



| type of electrolyte | $\varkappa$ | units of $V_R$ |
|---|---|---|
| 1 – 1 | $10^7$ | $ergs/cm^2$ |
|  | $10^6$ | $ergs \times 10^{-1}/cm^2$ |
|  | $10^5$ | $ergs \times 10^{-2}/cm^2$ |
|  | $10^4$ | $ergs \times 10^{-3}/cm^2$ |
| 2 – 2 | $10^7$ | $ergs/4\,cm^2$ |
|  | $10^6$ | $ergs \times 10^{-1}/4cm^2$ |
|  | $10^5$ | $ergs \times 10^{-2}/4cm^2$ |
|  | $10^4$ | $ergs \times 10^{-3}/4cm^2$ |
| 3 – 3 | $10^7$ | $ergs/9\,cm^2$ |
|  | $10^6$ | $ergs \times 10^{-1}/9cm^2$ |
|  | $10^5$ | $ergs \times 10^{-2}/9cm^2$ |
|  | $10^4$ | $ergs \times 10^{-3}/9cm^2$ |

Fig. 5. Repulsive potential as a function of $\varkappa d$, for strong interaction (small $\varkappa d$)

the force between the plates because it leads to an unexpectedly simple equation which can form the basis for a useful approximate expression for the repulsive potential.

Consider again two infinitely large flat plates with liquid between them, which liquid is in free contact with a reservoir containing an infinitely large amount of liquid at a pressure $p_0$ and a concentration of $n$ molecules of electrolyte per cm³. The electric potential of the reservoir is supposed to be zero. The plates are kept at a certain distance $d$ from each other by the exertion of a pressure $P$ per cm².

As the whole system is considered to be in equilibrium the gradient of the hydrostatic pressure and the force on the space charge balance each other at any point of the liquid phase.

$$dp + \rho \, d\psi = 0 \tag{19}$$

By introducing POISSON's equation and specializing to the space between the two parallel plates (19) may be transformed into

$$\frac{dp}{dx} - \frac{\varepsilon}{4\pi} \frac{d^2\psi}{dx^2} \frac{d\psi}{dx} = 0 \tag{20}$$

[1] I. LANGMUIR, *J. Chem. Phys.*, 6 (1938) 893.
[2] B. DERJAGUIN, *Trans. Faraday Soc.*, 36 (1940) 203.
[3] P. BERGMANN, P. LÖW-BEER, and H. ZOCHER, *Z. physik. Chem.*, A 181 (1938) 301.
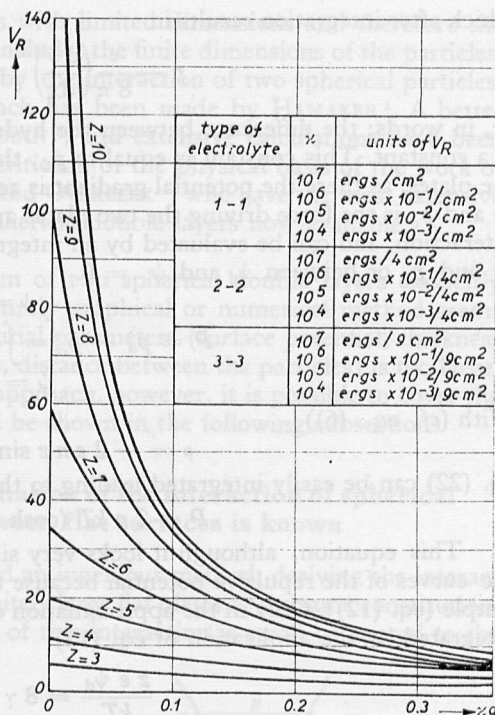
which after integration results in

$$p - \frac{\varepsilon}{8\pi}\left(\frac{d\psi}{dx}\right)^2 = \text{constant} \tag{21}$$

or, in words: the difference between the hydrostatic pressure and MAXWELL's stresses is a constant. This constant is equal to $p_d$, the hydrostatic pressure midway between the plates, as there the potential gradient is zero. The difference between this pressure $p_d$ and $p_o$ is the force driving the two plates apart as a consequence of the double layer interaction, and can be evaluated by an integration of eq. (19) between the pressures $p_d$ and $p_o$ or between $\psi_d$ and $\psi_o = 0$.

$$P = p_d - p_o = \int_{\psi = 0}^{\psi = \psi_d} dp = -\int_0^{\psi_d} \rho \, d\psi \tag{22}$$

With (cf. eq. (6))

$$\rho = -2\,e\,n\,z \sinh ze\,\psi/kT,$$

eq. (22) can be easily integrated leading to the result

$$P = 2\,n\,kT\,(\cosh ze\,\psi_d/kT - 1) \tag{23}$$

This equation, although it looks very simple, cannot be easily used to construct the curves of the repulsive potential because the relation between $\psi_d$ and $d$ is far from simple (eq. (12)). Only in the approximation of weak interaction can eq. (23) be easily integrated by the application of eq. (13)

$$\frac{z\,e\,\psi_d}{kT} = 8\,\gamma\,e^{-\varkappa d} \tag{13}$$

and the first approximation of eq. (23)

$$P = n\,kT\,(ze\,\psi_d/kT)^2 \tag{23'}$$

$$V_R = -2\int_\infty^d P\,dd = 64\,n\,kT\,\gamma^2\int_\infty^d e^{-2\varkappa d}\,d\,(2d) = \frac{64\,n\,kT}{\varkappa}\,\gamma^2\,e^{-2\varkappa d} \tag{24}$$

a relation [1] to which we shall return in the explanation of the rule of SCHULZE and HARDY (see chapter VIII).

## § 4.   THE INTERACTION OF TWO SPHERICAL DOUBLE LAYERS

### a.   General considerations

Although many characteristic features of the interaction of double layers, including a general survey of the conditions of the stability of hydrophobic colloids may be derived from our knowledge of the interaction of two infinitely large flat surfaces, in practical

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[1] A still somewhat more exact approximation is given by VERWEY and OVERBEEK, *Theory of the stability of lyophobic colloids*, p. 97 and is

$$V_R = \frac{32\,nkT}{\varkappa}\,\gamma^2\,(1 - \tanh \varkappa\,d) \tag{25}$$

cases one always has to do with particles with limited dimensions and therefore the need is felt for a model which essentially includes the finite dimensions of the particles. The most simple model, is then given by the interaction of two spherical particles.

A first, though rather crude, approach has been made by HAMAKER [1]. A better approximation has been given by DERJAGUIN [2], and extensive calculations have been published by LEVINE and DUBE [3]. For a criticism of the physical basis of the work of LEVINE and DUBE, however, see VERWEY and OVERBEEK [4], who gave the most extensive calculations on the interactions of two spherical double layers now available.

It is impossible to solve the problem of two spherical double layers explicitly because of mathematical difficulties. A purely graphical or numerical method seems unpromising because the number of essential parameters (surface potential, thickness of the double layer, radius of the particles, distance between the particles) is too large. By the application of diverse methods of approach, however, it is possible to cover the field of interest almost completely, as will be shown in the following subsections.

### b.   A general method for the estimation of the interaction of spherical particles, when that between flat surfaces is known

DERJAGUIN [5] has indicated and applied an ingenious method, deriving the interaction of spherical particles from that of infinitely large flat plates of the same constitution. His method is applicable when the range of this interaction is small compared to the radius of the particles. The surface of the spheres is divided into rings with their centers on the axis of symmetry as represented in Fig. 6.

Now the interaction of the spheres is built up from the interaction of these rings which are considered in pairs as rings cut out of two parallel flat plates. If the interaction energy of 1 cm² of two flat plates is denoted by $V(H)$, $H$ being the distance between the plates, the interaction of two rings with radius $h$ is given by



Fig. 6.   Illustrating the building up of the repulsion between two spheres out of the repulsion between quasi-parallel layers.

$$2 \pi h \, V(H) \, \mathrm{d}h \qquad (26)$$

By integration of this expression from $h = 0$ to $h = $ large, the total energy of interaction is found. As the value of the integrand for large values of $h$ is very small anyway (be-
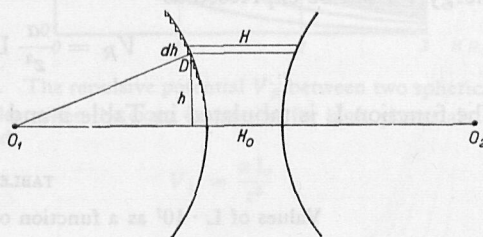
[1] H. C. HAMAKER, *Chem. Weekblad*, 35 (1938) 47 (*Cf.* also *Hydrophobic Colloids*, Amsterdam 1938, p. 16); *Rec. trav. chim.*, 55 (1936) 1015; 56 (1937) 3.

[2] B. DERJAGUIN, *Trans. Faraday Soc.*, 36 (1940) 203.

[3] S. LEVINE, *Proc. Roy. Soc. London*, A 170 (1939) 145, 165; S. LEVINE and G. P. DUBE, *Compt. rend.*, 208 (1939) 1812; *Trans. Faraday Soc.*, 35 (1939) 1125, 1141; 36 (1940) 215; S. LEVINE, *J. Chem. Phys.*, 7 (1939) 831; S. LEVINE and G. P. DUBE, *Phil. Mag.*, (7) 29 (1940) 105; *J. Phys. Chem.*, 46 (1942) 239.

[4] E. J. W. VERWEY and J. TH. G. OVERBEEK, *Theory of the stability of lyophobic colloids*, Amsterdam 1948, p. 188; *Trans. Faraday Soc.*, 42 B (1946) 117.

[5] B. DERJAGUIN, *Kolloid-Z.*, 69 (1934) 155; *Acta Physicochim. U.R.S.S.*, 10 (1939) 333; *Trans. Faraday Soc.*, 36 (1940) 203.

cause of the relatively small range of interaction), the upper limit may be chosen as $\infty$ which simplifies the calculation. In the same approximation $a\,\mathrm{d}H$ may be substituted for $2\,h\,\mathrm{d}h$ which leads to the following expression for the total energy of interaction $V_t$

$$V_t(H) = \pi\,a \int_{H_\circ}^{\infty} V(H)\,\mathrm{d}H \tag{27}$$

The nature of the forces between the particles is immaterial in this derivation provided their range is small enough.

### c. Application of Derjaguin's method to double layer interaction

Eq. (27) may be applied to double layer interaction when the range, which is of the order of $1/\varkappa$, is small in comparison with the radius ($a$) of the spheres, or when $\varkappa\,a \gg 1$. For the repulsive function between flat plates DERJAGUIN himself used our equation (25), the best approximation for small values of the surface potential.

The repulsive energy for two spheres is then found to be

$$V_R = \frac{\varepsilon\,a\,\psi_\circ{}^2}{2}\,\ln\left\{\,1 + \exp\left(-\varkappa\,H_\circ\right)\right\} \tag{28}$$

VERWEY and OVERBEEK [1] used the same method with the more exact expression (18) for the repulsion between flat plates, by means of which they derived that the repulsive energy $V_R$ can be expressed as

$$V_R = \frac{a}{z^2}\,\mathrm{L}\,(Z,\,\varkappa\,H_\circ) \tag{29}$$

The function L is tabulated in Table 3 and represented graphically in Fig. 7.

TABLE 3

Values of $\mathrm{L}\cdot 10^7$ as a function of $Z$ and $\varkappa\,H_\circ$, L being $\dfrac{z^2}{a}\,V_R$

| $\varkappa\,H_\circ$ \ $Z$ | 2 | 3 | 4 | 5 | 6 | 8 | 10 |
|---|---|---|---|---|---|---|---|
| 0 | 7.50 | 16.02 | 26.5 | 38.46 | 51.4 | 78.7 | 108.1 |
| 0.10 | 6.90 | 14.5 | 23.3 | 33.0$^5$ | 42.5 | 57.3 | 66.9 |
| 0.20 | 6.35 | 13.1 | 20.7$^5$ | 28.6 | 35.6 | 45.0 | 51.1 |
| 0.30 | 5.85 | 11.9 | 18.61 | 24.92 | 30.5 | 37.0 | 40.9 |
| 0.50 | 4.96 | 9.78 | 14.85 | 19.36 | 23.0 | 26.9$^5$ | 29.3 |
| 0.70 | 4.06 | 7.98 | 11.96 | 15.31 | 17.93 | 20.7 | 22.2 |
| 1.00 | 3.04 | 5.91 | 8.73 | 11.06 | 12.72 | 14.5 | 15.44 |
| 1.20 | 2.54 | 4.86 | 7.13 | 8.92 | 10.23 | 11.5 | 12.33 |
| 1.50 | 1.91$^5$ | 3.67 | 5.29 | 6.59 | 7.56$^5$ | 8.54 | 8.99 |
| 2.00 | 1.16$^5$ | 2.37 | 3.25 | 4.03 | 4.59 | 5.17 | 5.40 |
| 2.50 | 0.71 | 1.44 | 2.08 | 2.46 | 2.94 | 3.16 | 3.35 |
| 3.00 | 0.43 | 0.86$^5$ | 1.25 | 1.53 | 1.78 | 1.95 | 2.05$^5$ |

[1] loc. cit. p. 140.

Without going into details, which will be considered in § 10 and in chapter VIII, we draw attention to the fact that the interaction is proportional to the radius of the sphere and not to its square as might on first sight be expected.

### d. The interaction of two spheres when the double layer thickness is large

When the spherical particles are small in comparison with the thickness of the double layer, the method treated in the foregoing subsections breaks down completely, and another approach becomes necessary.

For this case a method has been used by VERWEY and OVERBEEK [1], consisting in a calculation of the distribution of charge and potential around two spherical particles and a derivation of the free energy of the double layer system by application of eq. (1). A drawback of this method is that it is only accurate if the surface potential is small, but a more general method is not yet available.

Fig. 7. The repulsive potential $V_R$ between two spherical particles, when the exact expression for high potentials is applied

$$V_R = \frac{a\,L}{z^2}$$

The results are represented graphically in Fig. 8. For complete calculations and an extensive tabular review of the results the reader is referred to the original publication.

Again, as in the case when $\varkappa\,a \gg 1$ the repulsive energy is proportional to the radius of the particles and of course is larger, the larger the potential of the surface.

### e. Survey of the choice of the method to be applied in actual calculations on spherical particles

As it would lead us too far to repeat the discussion on the regions of validity of the different approximations given by VERWEY and OVERBEEK [2] — but on the other hand an indication of the different limits of validity should be useful for future applications — we give without proof an enumeration of the methods to be applied in the form of a table.
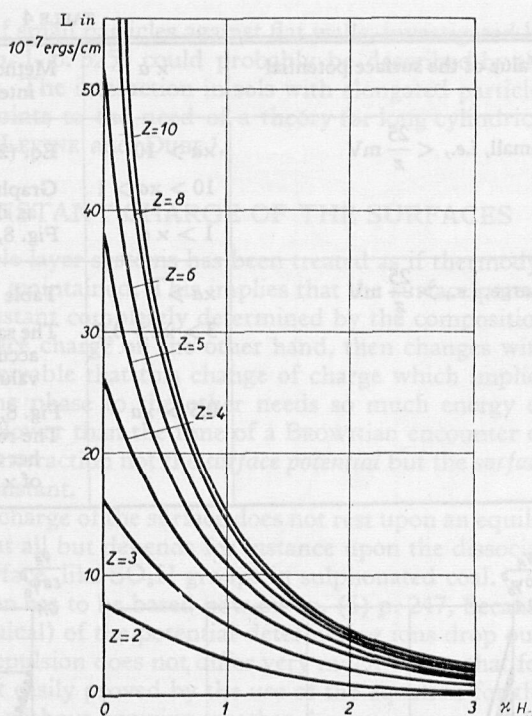
[1] loc. cit., p. 143.
[2] loc. cit., p. 139, 156.

TABLE 4

| Value of the surface potential | $\kappa a$ | Method to be applied for the calculation of the interaction of two spherical double layers. |
|---|---|---|
| Small, i.e., $< \dfrac{25}{z} mV$ | $\kappa a > 10$ | Eq. (28) |
| | $10 > \kappa a > 1$ | Graphical compromise between eq. (28) and Fig. 8, as illustrated in Fig. 9 for $\kappa a = 3$. |
| | $1 > \kappa a$ | Fig. 8, § 4 d. |
| Large, i.e., $> \dfrac{25}{z} mV$ | $\kappa a > 3$ | Table 3, Fig. 7. |
| | $3 > \kappa a > 0,5$ | The same, but the results become less accurate. The accuracy is more favourable, the higher the value of the surface potential. |
| | $0,5 > \kappa a$ | Fig. 8, § 4 d.<br>The results become less and less accurate, the higher the surface potential, and the higher the value of $\kappa a$. |
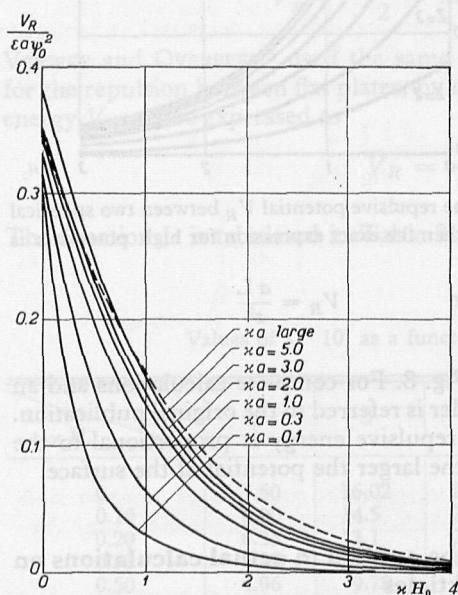


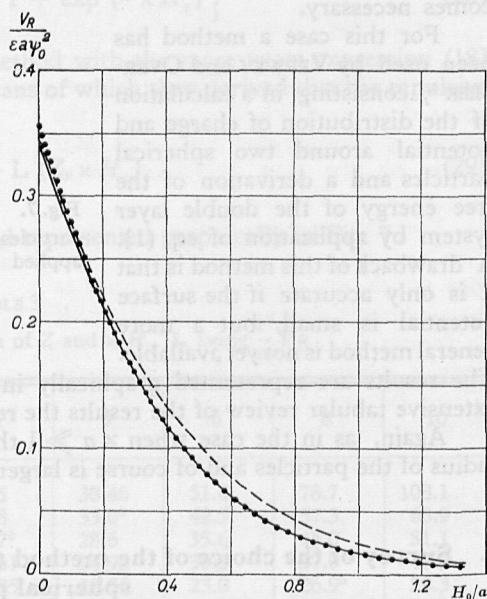Fig. 8. Potential energy of repulsion between two spherical particles for different values of $\kappa a$

Fig. 9. Repulsion curves for $\kappa a = 3$
----- equation (28)
........ Fig. 8
——— best curve

# § 5.   INTERACTION FOR OTHER FORMS OF PARTICLES

Although the essential features of double layer interaction are quite clearly given by the cases of flat and spherical double layers, in practical applications other forms

may be of interest. The coagulation of small particles against flat walls, investigated by voN Buzagh (see chapter VIII, § 7 b. 1, p. 325) could probably be described by the interaction of spheres with flat plates. The interaction in sols with elongated particles (*e.g.*, $V_2O_5$, tobacco mosaic virus) points to the need of a theory for long cylindrical particles. This has been treated by Levine and Dube [1].

## § 6.    INTERACTION AT CONSTANT CHARGE OF THE SURFACES

Thus far the interaction of double layer systems has been treated as if thermodynamic equilibrium were continuously maintained. This implies that the surface potential, $\psi$ , has been considered as a constant completely determined by the composition of the electrolytic solution. The surface charge on the other hand, then changes with the interaction. Now it is quite conceivable that this change of charge which implies transition of charge carriers from one phase to the other needs so much energy of activation, that the process is much slower than the time of a Brownian encounter of two particles. In that case during the interaction not the *surface potential* but the *surface charge* should be considered as a constant.

The same is applicable when the charge of the surface does not rest upon an equilibrium of potential-determining ions at all but depends for instance upon the dissociation of certain groups fixed at the surface, like $SO_3H$ groups in sulphonated coal.

The whole treatment of interaction has to be based now on eq. (5) p. 247, because the contributions (electrical and chemical) of the potential-determining ions drop out. Fortunately, however, the resulting repulsion does not differ very much [2] from that for constant potential which may be most easily proved by the use of the equation for the repulsive forse (23), which is derived without knowing whether during interaction the charge or the potential of the surface is kept constant.

When therefore in the following part the treatment is restricted to the case of constant potential this is practically no restriction, constant potential and constant charge leading to almost the same results.

## § 7.    INTERACTION OF TWO DOUBLE LAYERS AT THE INTERFACE BETWEEN TWO LIQUIDS. CASE OF EMULSIONS

In chapter IV, § 4c, p. 128 it has been shown that the double layer at the interface of two liquids has a diffuse character in both phases. When one of the phases is an "oil" with low dielectric constant and the other phase consists of water, the major part of the potential drop occurs in the oil phase.

The interaction of two double layers of this type has a twofold interest.

1. In an emulsion, that is a dispersion of small liquid drops in another liquid, the diameter of the drops may easily be so small that in the interior of the drops the two double layers generated on opposite poles of the drops interfere. This causes, as has been explained in § 3a, p. 247, a lowering of the charge of the double layer and conse-

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[1] G. P. Dube, *Indian J. Phys.*, 17 (1943) 189; see also: S. Levine, *Trans. Faraday Soc.*, 42 B (1946) 102.

[2] In fact, the repulsion at constant charge is slightly larger than that of constant potential.

quently a decrease of the potential drop in the outer phase. This effect is illustrated in Fig. 10, where the electric potential in a system consisting of a thin layer of an "oil" between two water layers has been reproduced [1].

The potential drop in the water phase, already small when the oil phase is thick, becomes still smaller when the oil is present in the form of a thin layer.

2. In the second place the interaction of the double layers of two droplets of an emulsion will determine the stability of the emulsion. A complete description of this effect offering still more mathematical difficulties than the interaction of two spherical double layers as treated in § 4 will not be aimed at, as a superficial consideration will already be sufficient to demonstrate that the energy of interaction between two droplets of an emulsion is much smaller than that between solid particles. This explains why emulsions of two pure liquids are never stable (*cf*. chapter VIII, § 11, p. 336) and why the addition of emulsifiers is necessary to prepare stable emulsions.

Let us first consider the meeting of two drops (radius $a$) of water in a continuous oil phase. In that case the repulsive energy will be of the order of (*cf*. eq. (28))

$$V_R \backsim \varepsilon_{oil} \, a \, \psi^2_{oil}$$

in which $\varepsilon_{oil}$ and $\psi_{oil}$ are the dielectric constant and the potential drop in the oil. As $\varepsilon_{oil} \ll \varepsilon_{water}$, this repulsion is much smaller than that between solid particles in water, although $\psi_{oil}$ may be fairly large.

When on the contrary two oil drops in a water phase approach each other, the work of interaction will be about

$$V_R \backsim \varepsilon_{water} \, a \, \psi^2_{water}$$

and as to a first approximation

$$\frac{\psi_{water}}{\psi_{oil}} = \sqrt{\frac{n_\circ \, \varepsilon_\circ}{n_w \, \varepsilon_w}} \tag{29}$$

where $n_\circ$ and $n_w$ are the concentrations of monovalent electrolytes in the two phases, the repulsive energy becomes

$$V_R \backsim \varepsilon_w \, a \, \psi^2_w = \varepsilon_\circ \, a \, \psi^2_\circ . \frac{n_\circ}{n_w}$$

which, as $n_\circ$ will usually be much smaller than $n_w$, is still smaller than the repulsive energy between two water droplets in oil.
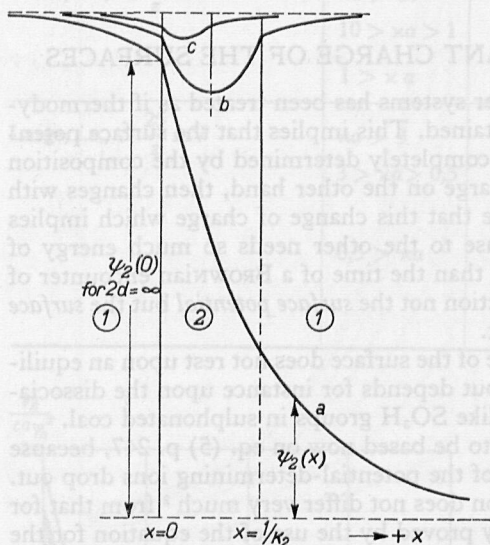


Fig. 10. The interaction of two double layers at the interface liquid/liquid. Phase 2 is the phase with the lowest dielectric constant ("oil"). Curve $a$: both phases infinitely thick; curve $b$: the oil phase has a thickness $2d = 1/\varkappa_{oil}$; curve $c$: the oil phase has a thickness $2d = 1/2\varkappa_{oil}$.

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[1] E. J. W. VERWEY, *Trans. Faraday Soc.*, 36 (1940) 192.

## § 8.   INFLUENCE OF THE STERN CORRECTION ON THE INTERACTION

In order to complete the picture of the interaction of double layers, it is still necessary to take account of the finite dimensions and the specific adsorbability of the ions as introduced by STERN [1] (*cf.* chapter IV, § 4b, p. 127).

It has been mentioned in chapter IV, that the picture given by STERN should only be considered as a provisional one, but experimental data from very different fields (electrocapillary curve, chapter IV, § 5, p. 146, adsorption isotherms of potential determining ions, chapter IV, § 6, p. 162, electrophoresis, chapter V, § 9b. 1, p. 226, stability, chapter VIII, § 4, p. 310) indicate that the GOUY-CHAPMAN theory of the double layer becomes insufficient when either the potential or the electrolyte content is high.

Retaining for the moment STERN's theory it should be asked how the interaction is modified by the presence of a STERN layer. Considering again two flat plates approaching each other, the primary effect will be an interaction of the two diffuse double layers, *cf.* Fig. 11. A direct influence of the two STERN layers on each other will only occur when the distance between the plates becomes of the order of atomic dimensions and thus may usually be left out of consideration.

Fig. 11.  Interaction of the diffuse parts of two double layers consisting each of a STERN layer and a diffuse layer.

The first effect of the interaction is a decrease of the charge of the diffuse double layer, but, as is confirmed by a more detailed calculation [2] when the interaction is not very strong the potential of the STERN layer $\psi_\delta$ will be practically unaffected.

This being the case, the whole interaction between two double layers may then be described by the methods described in § 3 and § 4, with the only modification that the surface potential $\psi_o$ has to be replaced by the STERN potential $\psi_\delta$, the value of which may be determined from the distribution of the double layer on one plate only.

For considerations on the stability of colloids this implies the following important points.

1. As $\psi_\delta$ is usually smaller than $\psi_o$, the very high potentials in the double layer, where the applicability of BOLTZMANN's principle in its simple form [3] is questionable, are eliminated.
2. Even if $\psi_o$ is (or is nearly) independent of the concentration of indifferent electrolytes, $\psi_\delta$ will strongly depend upon it (*cf.* chapter IV, § 4d, Fig. 5, p. 131) and in comparing the stability for different contents of electrolyte this effect should be taken into account.
3. Although in the diffuse double layer only the concentration and valency of the ions are important, the value of the STERN potential $\psi_\delta$ is determined by specific properties of the ions, and this enables us to explain differences in the stability between ions of the same valency type.

Especially for this last-mentioned reason a further development of STERN's ideas would seem well worth the trouble.
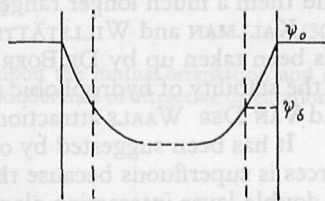
[1] O. STERN, *Z. Elektrochem.*, 30 (1924) 508.

[2] E. J. W. VERWEY and J. TH. G. OVERBEEK, *loc. cit.*, p. 128.

[3] *cf.* chapter IV, § 4a p. 126.

## § 9. ATTRACTIVE FORCES BETWEEN COLLOIDAL PARTICLES

### a. Long range character of the London-Van Der Waals attraction

In order to understand colloid stability, besides the double layer repulsion an attraction which keeps the coagulum together must be assumed to exist. This attraction must be of a very general kind because all lyophobic suspensions can be made to coagulate by removing the double layer repulsion. The only known attractive forces of sufficient generality are the LONDON dispersion forces. Usually the LONDON-VAN DER WAALS forces are supposed to have only a very short range, of the order of atomic dimensions. In the case of colloidal particles the additivity of dispersion forces, however, lend them a much longer range (of the order of colloidal dimensions).

KALLMAN and WILLSTÄTTER [1] were the first to draw attention to this fact. The idea has been taken up by DE BOER [2] and especially by HAMAKER [3] who developed a theory of the stability of hydrophobic colloids based on the interplay of double layer repulsion and VAN DER WAALS attraction.

It has been suggested by other authors [4] that the introduction of VAN DER WAALS forces is superfluous because the attraction can already be explained by the properties of double layer interaction alone. As the criticism [5] on this point of view has not been refuted satisfactorily [6] for the time being the only origin of the attraction is to be found in the VAN DER WAALS forces.

### b. Van Der Waals attraction between two atoms

The attraction between two neutral atoms, already introduced in 1873 by VAN DER WAALS [7] to explain the properties of non-ideal gases and liquids, has been explained by three different effects. Two of them, the interaction of the dipole moments [8] and the polarizing [9] action of a dipole in one molecule on the other molecule can be understood on the lines of classical physics. LONDON [10] however showed that also between apolar atoms an attraction exists which is a typical quantum mechanical effect, and which, in all cases except for extremely polar molecules like $H_2O$ or $NH_3$, is stronger than the DEBYE and the KEESOM effect.

The LONDON force may be visualized by the following correspondence picture. In a neutral atom the zero point energy of the electrons generates a rapidly fluctuating dipole

[1] H. KALLMANN and M. WILLSTÄTTER, *Naturwissenschaften*, 20 (1932) 952.

[2] J. H. DE BOER, *Trans. Faraday Soc.*, 32 (1936) 21.

[3] H. C. HAMAKER, *Rec. trav. chim.*, 55 (1936) 1015; 56 (1937) 3, 727.

[4] I. LANGMUIR, *J. Chem. Phys.*, 6 (1938) 893; S. LEVINE, *Trans. Faraday Soc.*, 42 B (1946) 102.

[5] B. DERJAGUIN, *Acta Physicochimica U.R.S.S.*, 10 (1939) 333; *Trans. Faraday Soc.*, 36 (1940) 203; B. DERJAGUIN, *Acta Physicochimica U.R.S.S.*, 12 (1940) 181, 314; B. DERJAGUIN and L. D. LANDAU, *Acta Physicochim. U.R.S.S.*, 14 (1941) 633; E. J. W. VERWEY, *Philips Research Repts.*, 1 (1945) 33; E. J. W. VERWEY and J. TH. G. OVERBEEK, *Trans. Faraday Soc.*, 42 B (1946) 117; *Theory of the stability of lyophobic colloids*, Amsterdam 1948.

[6] See General Discussion, *Trans. Faraday Soc.*, 42 B (1946) 123 et seq.

[7] J. D. VAN DER WAALS, *Thesis*, Leyden 1873; *Die Kontinuität des gasformigen und flüssigen Zustande*-I, II, Leipzig 1899.

[8] W. H. KEESOM, *Proc. Koninkl. Nederland Akad. Wetenschap*, 18 (1915) 636; 23 (1920) 939; *Physik. Z.*, 22 (1921) 129, 643.

[9] P. DEBYE, *Physik. Z.*, 21 (1920) 178; 22 (1921) 302.

[10] F. LONDON, *Z. Physik.*, 63 (1930) 245; See also H. MARGENAU, *Revs. Modern Phys.*, 11 (1939) 1.

moment. The frequency of the fluctuation is of the order of the frequency of electronic movements, *i.e.*, of the order of $10^{15}$ or $10^{16}$ per second. The fluctuating dipole of one atom polarizes the other one and consequently the two atoms attract each other.

The three components of the VAN DER WAALS attraction all give rise to an attractive energy varying inversely as the sixth power of the distance between the two atoms.

The potential of a dipole at a distance $r$ is equal to

$$\psi = \frac{\mu \cos \vartheta}{r^2}$$

where $\vartheta$ is the angle between the dipole moment and the radius vector. So the field strength $F$ is proportional to $\frac{1}{r^3}$ and the DEBYE interaction with a molecule whose polarizability is $\alpha$

$$V_{\text{DEBYE}} = -\frac{1}{2} \alpha F^2 \sim -\frac{\alpha \mu^2}{r^6} \tag{30}$$

The energy of interaction, $\varepsilon$, between two dipoles depends upon the mutual orientation and is proportional to $\mu^2/r^3$. The KEESOM attraction results from the preponderance of attractive orientations over repulsive ones due to the BOLTZMANN principle.

$$V_{\text{KEESOM}} = \frac{\displaystyle\int_{\substack{\text{over all} \\ \text{orientations}}} \varepsilon \, e^{-\varepsilon/kT} \, \mathrm{d}\psi \, \mathrm{d}\vartheta}{\displaystyle\int_{\substack{\text{over all} \\ \text{orientations}}} e^{-\varepsilon/kT} \, \mathrm{d}\psi \, \mathrm{d}\vartheta}$$

$$\sim -\frac{\varepsilon^2}{kT} \sim -\frac{\mu^4}{kT \cdot r^6} \tag{31}$$

Finally the LONDON energy can, according to the above mentioned correspondence principle, be described as a sort of DEBYE effect and consequently is also proportional to $\frac{1}{r^6}$. Various authors have developed approximate expressions for the proportionality factor of which we cite here without proof LONDON's own equation.

$$V_{\text{LONDON}} = -\frac{\frac{3}{4} \alpha^2 h \nu}{r^6} \tag{32}$$

in which $h\nu$ is a characteristic energy corresponding to the chief dispersion frequence $\nu$ taken from the dispersion spectrum of the atom.

Alternative approximations have been given by SLATER and KIRKWOOD [1] and by NEUGEBAUER [2] leading to somewhat different (mostly higher) numerical values.

A fundamental difference between the KEESOM and DEBYE energy on one hand and the LONDON energy on the other hand appears when the attractive forces between conglomerations of atoms are considered as will be neccessary for the application to colloid phenomena. As the electric field strength acting on an atom is the vectorial sum of the separate field strengths generated by each of the other atoms, the total energy of interaction due to the KEESOM and the DEBYE forces is not equal to the sum of the separate interaction energies but usually much smaller. The LONDON energy between two atoms, however, is to the first approximation independent [3] of the interaction with other atoms. So for a large number of atoms the total LONDON energy may be found by a simple summation which for many cases may even be replaced by an integration (see next section).

[1] J. C. SLATER and J. G. KIRKWOOD. *Phys. Rev.*, 37 (1931) 682.
[2] TH. NEUGEBAUER, *Z. Physik*, 107 (1937) 785.
[3] See for instance H. HELLMANN, *Einführung in die Quantenchemie*, Leipzig und Wien, 1937, p. 189.

### c.  Retardation of London-Van Der Waals forces

As the LONDON forces are essentially of electric origin, a certain time is necessary for their propagation and it can be expected that a more complete treatment, taking account of relativistic effects, may change the laws of interaction. If indeed the correspondence picture of the previous subsection is followed more closely, it would be expected that if the time of travel of an electromagnetic wave from one atom to the other is of the same order or larger than the time of revolution of the electrons, or, which amounts to the same thing, if the distance between two atoms is comparable with the wave length of the LONDON frequency (cf. eq. 32), the LONDON force will be smaller than the value given by eq. (32).

This qualitative picture has been worked out by CASIMIR and POLDER [1] who found that for large distances between the atoms the LONDON energy decreases as $\frac{1}{r^7}$ instead of as $\frac{1}{r^6}$.
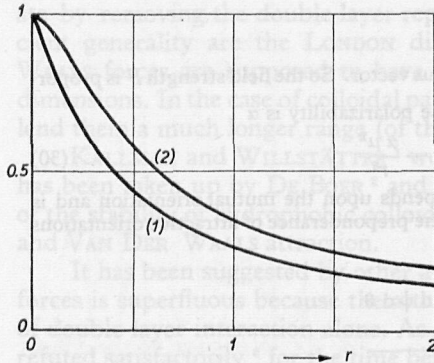


Fig. 12. Correction factor due to retardation for the contribution of one excited state to the usual LONDON energy. (1) For the interaction between a neutral atom and a metallic wall. $r$ is measured in units $\frac{1}{2}\lambda$ (2) For the interaction between two neutral atoms. $r$ is measured in units $\lambda$.

Fig. 12 shows how, in an especially simple case, the LONDON interaction is weakened by this retardation effect and how this weakening begins to be important when the distance of the two atoms is of the order of $\lambda$ which may be estimated as 1000 Å or thereabouts.

The correction function can be quite accurately represented by simple analytical expressions, namely

$$V = - \frac{^3/_4 \, \alpha^2 \, h\nu}{r^6} \, f(p) \tag{33}$$

in which $p = 2\pi \frac{r}{\lambda}$, $\lambda = \frac{c}{\nu}$

$$0 < p < 3 \qquad f(p) = 1.01 - 0.14\,p$$

$$3 < p < \infty \qquad f(p) = \frac{2.45}{p} - \frac{2.04}{p^2}$$

### § 10.  LONDON-VAN DER WAALS ATTRACTION BETWEEN TWO PARALLEL FLAT PLATES

#### a.  Attraction according to the inverse sixth power law

Consider two infinitely large flat plates, each of thickness $\delta$, at a distance $2\,d$ from each other. The number of atoms per cm³ is $q$ and the LONDON energy between two atoms at a distance $r$
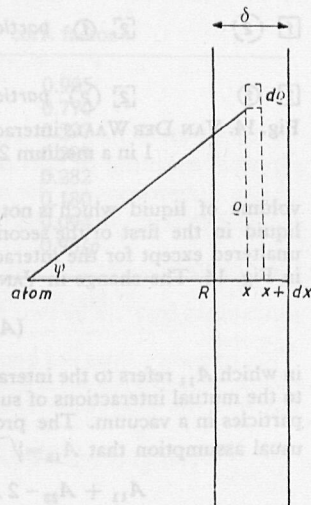
$$V_{\text{LONDON}} = - \frac{\beta}{r^6} \tag{34}$$

[1] H. B. G. CASIMIR and D. POLDER, Phys. Rev., 73 (1948) 360; Nature, 158 (1946) 787.

Then the attractive energy per cm² of the two plates can be easily calculated. When the distance $d$ is larger than a few atomic diameters the summation of (34) over all atomic pairs may be replaced by an integration.

In Fig. 13 an atom (belonging to the left hand plate) is sketched in its interaction with the other plate. The right hand plate is thought to be built up of infinitesimal small rings of diameter $\varrho$, cross section $d\varrho\ dx$ at a distance $(R + x)$ from the atom considered.

The energy of interaction is found equal to

$$f = \int_0^\delta \int_0^\infty -2\,\pi\,\varrho \cdot d\varrho \cdot dx \cdot q \cdot \frac{\beta}{\{(R + x)^2 + \varrho^2\}^3} =$$

$$= -\frac{\pi \beta q}{6}\left(\frac{1}{R^3} - \frac{1}{(R + \delta)^3}\right) \qquad (35)$$

The interaction of a column with cross-section $dO$ and a length equal to the thickness of the second plate is given by

$$V_A\,dO = \int_{2d}^{2d+\delta} dO \cdot d\,R \cdot q \cdot f = -\frac{A}{48\,\pi}\left\{\frac{1}{d^2} - \frac{1}{(d + \delta)^2}\right. -$$

$$\left. -\frac{2}{\left(d + \dfrac{\delta}{2}\right)^2}\right\}\,dO \qquad (36)$$

Fig. 13. Illustrating the LONDON-VAN DER WAALS forces between an atom and an infinitely large plate of thickness $\delta$.

in which, following HAMAKER, $A$ is written for $\pi^2\,q^2\,\beta$.

When the distance between the plates is small compared with their thickness the energy of attraction per cm² simplifies to

$$V_A = -\frac{A}{48\,\pi\,d^2} \qquad (37)$$

This attraction decays comparatively slowly with increasing distance, a property explaining the long range character of the LONDON-VAN DER WAALS forces. For very small distances the attractive energy tends to assume an infinitely large negative value. But there, of course, the approximation used is not valid. In addition to it not being permissible to substitute the integration process for the summation over all pairs of atoms repulsive forces will also come into action due to the BORN-repulsion between the electronic clouds. It does not seem worth while to try to correct equation (37) for these effects as physical surfaces probably always possess a certain surface roughness [1] exceeding molecular dimensions, so that a treatment of perfectly flat surfaces at very small distances apart is senseless.

For the applications of VAN DER WAALS forces to colloid science fortunately the most interesting distances are much larger than atomic dimensions and therefore these difficulties form no obstacle.

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[1] *Cf.* J. J. BIKERMAN, *Surface chemistry for industrial research*, New York 1947.

In most practical cases the colloidal particles are not separated by a vacuum, but are embedded in a medium (*e.g.*, water). The quantity A has then to be replaced by a more complicated expression, which, however, is independent of form and distance of the particles and is always positive [1].

1 2      2 1   *particles far apart*

1 1      2 2   *particles side by side*

Fig. 14. VAN DER WAALS interaction of particles 1 in a medium 2.

In Fig. 14 we consider the interaction between two particles of substance 1 embedded in substance 2 at two different distances. One particle is sketched as a square one, the other as a round one. When the round particle is brought nearer to the square one, inevitably an equal volume of liquid is displaced and taken farther away from the square particle. In order to evaluate all the energies involved, it is necessary to consider a "square" volume of liquid which is not displaced and which is near the round particle or the round volume of liquid in the first or the second situation. The VAN DER WAALS energy of the whole system remains unaltered except for the interactions between the two particles and the two volumes of liquid sketched in Fig. 14. The change in VAN DER WAALS energy between the two situations is given by

$$(A_{11} + A_{22} - 2 A_{12}) \int \int \frac{dV_{square} \cdot dV_{round}}{r^6}$$

in which $A_{11}$ refers to the interaction of atoms 1 among each other, $A_{22}$ to that among atoms 2, and $A_{12}$ to the mutual interactions of substance 1 and substance 2. The volume integral is the same as for two particles in a vacuum. The proportionality constant $A_{11} + A_{22} - 2 A_{12}$ is always positive when the usual assumption that $A_{12} = \sqrt{A_{11} \cdot A_{22}}$ may be used, for then

$$A_{11} + A_{22} - 2 A_{12} = A_{11} + A_{22} - 2\sqrt{A_{11} \cdot A_{22}} = (\sqrt{A_{11}} - \sqrt{A_{22}})^2$$

The influence of the medium through which the LONDON forces are transmitted would be taken into account by dividing $A$ by the dielectric constant of the medium for a suitable frequency. As, however, we are anyway badly informed on the values of the LONDON interaction of the substances which are important in colloid chemistry we shall not discuss this correction any further.

To give an idea as to the order of magnitude of $A$ we give the value calculated according to the method of SLATER-KIRKWOOD [2] for the $A_{water-water}$, which is found equal to

$$A_{w.w.} = 0 - 6 \times 10^{-12}.$$

# b. Introduction of the retardation correction

The retardation correction to the LONDON attraction between flat plates is found by introducing the retardation correction to the attraction of two atoms ( § 9c, p. 266) in the considerations of the preceding subsection. In § 9c the retardation correction has been given in terms of $2\pi r/\lambda$ ( $\lambda$ = LONDON-wavelength). When the distance between the plates is much larger than $\lambda$, only that part of the LONDON attraction which varies as $\dfrac{1}{r^7}$ is felt.

This leads us to an attraction between two plates (infinitely thick) decaying as $1/d^3$ instead of as $1/d^2$ (*cf.* eq. 37).

The whole corrected attraction function is easily found by the application of eq. (33) and is represented in Fig. 15 and Table 5.

[1] H. C. HAMAKER, *Physica*, 4 (1937) 1058.
[2] J. C. SLATER and J. G. KIRKWOOD, *Phys. Rev.*, 37 (1931) 682.

TABLE 5

Correction factor to be applied to the LONDON attraction between two flat plates in order to account for the retardation effect

$$V_{att} = \frac{A}{48\,\pi\,d^2} \times \text{corr. factor}$$

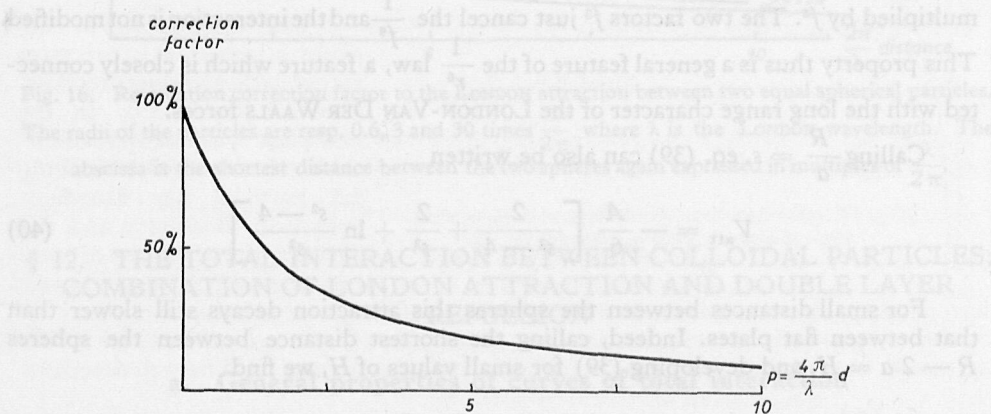| $p = 4\,\pi\,d/\lambda$ | corr. factor |
|---|---|
| 0.2 | 0.905 |
| 0.5 | 0.770 |
| 1.0 | 0.597 |
| 2.0 | 0.389 |
| 3.0 | 0.282 |
| 5.0 | 0.180 |
| 10.0 | 0.094 |
| large | 0.98/p |



Fig. 15. Retardation correction factor to the LONDON attraction between two flat plates at a distance 2d.

In a special case, *viz.*, that of two perfectly conducting plates CASIMIR[1] derived the value of the retarded LONDON attraction in a completely independent way and came to following expression for the attractive force $F$, valid for large values of $d$ (expressed in microns)

$$F = 0.013 \, \frac{1}{d^4} \; \text{dyne/cm}^2 \tag{38}$$

in good accord with his former work and the above given value for plates of arbitrary material.

## § 11.   LONDON ATTRACTION BETWEEN TWO SPHERES

In principle the calculation of the LONDON attraction between two spheres follows the same lines as that between flat plates, only the integrations to be carried out are somewhat more intricate.

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[1] H. B. G. CASIMIR, *Proc. Koninkl. Nederland Akad. Wetenschap*, 51 (1948) 793.

The problem has been resolved by HAMAKER [1] for the interaction of two spheres of arbitrary dimensions at an arbitrary distance.

His result, specialized for the case of two equal spheres of radius $a$ with a distance $R$ between their centres, is given by

$$V_{\text{att}} = -\frac{A}{6}\left[\frac{2\,a^2}{R^2-4\,a^2}+\frac{2\,a^2}{R^2}+\ln\frac{R^2-4\,a^2}{R^2}\right] \tag{39}$$

This attraction can be described as a function of the ratio between $R$ and $a$. The physical meaning of this is clear. The attractive energy retains the same value when all the dimensions of the system are multiplied by the same factor. Then all the distances between corresponding interacting volume elements are multiplied by a factor, $f$, the interacting energy is multiplied by $\frac{1}{f^6}$ but the volume elements themselves are each multiplied by $f^3$. The two factors $f^3$ just cancel the $\frac{1}{f^6}$ and the interaction is not modified This property thus is a general feature of the $\frac{1}{r^6}$ law, a feature which is closely connected with the long range character of the LONDON-VAN DER WAALS forces.

Calling $\frac{R}{a}=s$, eq. (39) can also be written

$$V_{\text{att}} = -\frac{A}{6}\left[\frac{2}{s^2-4}+\frac{2}{s^2}+\ln\frac{s^2-4}{s^2}\right] \tag{40}$$

For small distances between the spheres this attraction decays still slower than that between flat plates. Indeed, calling the shortest distance between the spheres $R-2\,a=H$, and developing (39) for small values of $H$, we find

$$V_{\text{att}} = -\frac{Aa}{12}\,\frac{1}{H} \tag{41}$$

whereas of course for large distances between the spheres $V_{\text{att}}$ decays as $\frac{1}{R^6}$.

The eq. (39) and (40) are valid only if the retardation is neglected. If we want to introduce the retardation correction this can be done in the same way as for the flat plates. The integrations are rather tedious though in principle not difficult. The results are given in Fig.16 which represents the ratio between the LONDON force with retardation and that following the reciprocal sixth power law. As the retardation depends explicitly on the length $\lambda$, it is now impossible to express the results as a simple function of $\frac{R}{a}$. In Fig. 16 we have therefore chosen as abscissa the separation between the two spheres $H=R-2a$ expressed as a multiple of $\frac{\lambda}{2\,\pi}$. The different curves are valid for spheres of different magnitude, the smallest giving the same correction function as that between single atoms, the largest resembling more and more the case of flat plates.

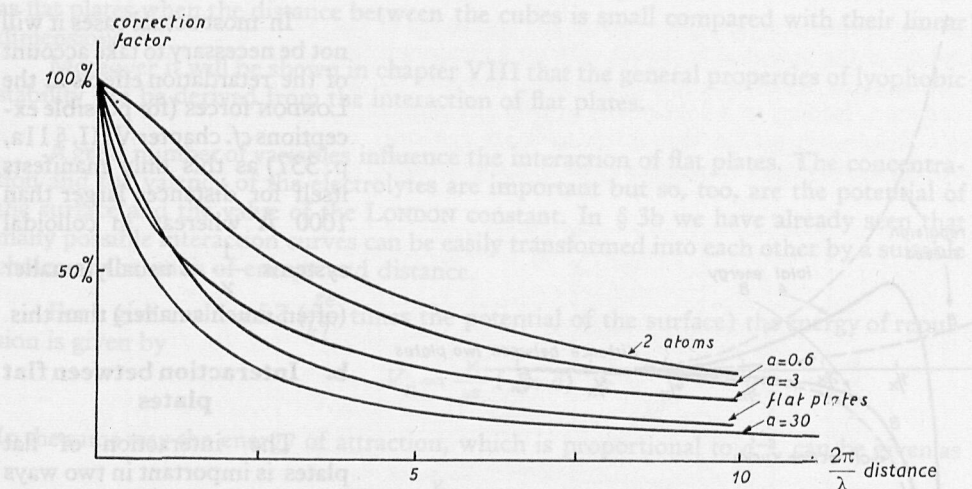[1] H. C. HAMAKER, *Physica*, 4 (1937) 1058.

Fig. 16. Retardation correction factor to the LONDON attraction between two equal spherical particles. The radii of the particles are resp. 0.6, 3 and 30 times $\dfrac{\lambda}{2\pi}$ where $\lambda$ is the LONDON-wavelength. The abscissa is the shortest distance between the two spheres again expressed in multiples of $\dfrac{\lambda}{2\pi}$.

## § 12. THE TOTAL INTERACTION BETWEEN COLLOIDAL PARTICLES; COMBINATION OF LONDON ATTRACTION AND DOUBLE LAYER REPULSION

### a. General properties of curves of total interaction

The total energetic interaction between colloidal particles is found by addition of the repulsion and the attraction curves. The general character of this curve of total interaction can be easily deduced from the properties of the repulsion and the attraction. The repulsion has the features of an exponential function with a range of the order of the thickness of the double layer. It remains finite for all values of the distance between the particles. The attraction however decreases as some inverse power of the distance. For very small distances it goes to very large negative values. Consequently the attraction will predominate at very small and at very large distances. At intermediate distances the repulsion may predominate but whether this is really the case will depend upon the actual numerical values of attraction and repulsion. In principle there are two different types of curves of total interaction, *viz.*, one with a maximum at intermediate distances and a minimum at larger distances and the other showing a monotonic decrease of the energy with decreasing distance. See Fig. 17. The separation between the particles at which these maxima and minima occur will be of the order of magnitude of the thickness of the electrical double layer, as this is the range of the repulsion.

In Fig. 18 one attraction curve is combined with a number of repulsion curves of different range, which shows very clearly the displacement of the maximum to larger distances with decreasing concentration of electrolytes (increasing $\dfrac{1}{\varkappa}$).
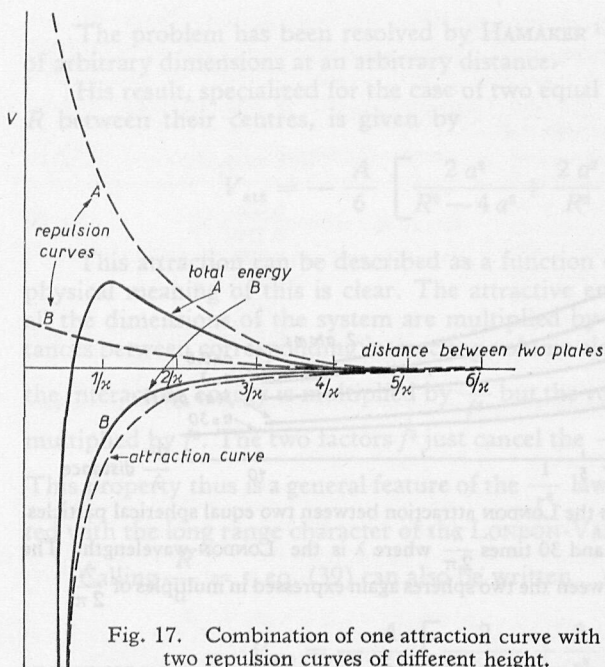
In most actual cases it will not be necessary to take account of the retardation effects in the LONDON forces (for possible exceptions cf. chapter VIII, § 11a, p. 337) as this only manifests itself for distances larger than 1000 Å whereas in colloidal systems $\frac{1}{\varkappa}$ is usually smaller (often much smaller) than this.

## b. Interaction between flat plates

The interaction of flat plates is important in two ways for our understanding of colloid-chemical phenomena. In the first place it can be applied immediately to systems containing flat particles like vanadium pentoxide, bentonite and the like. But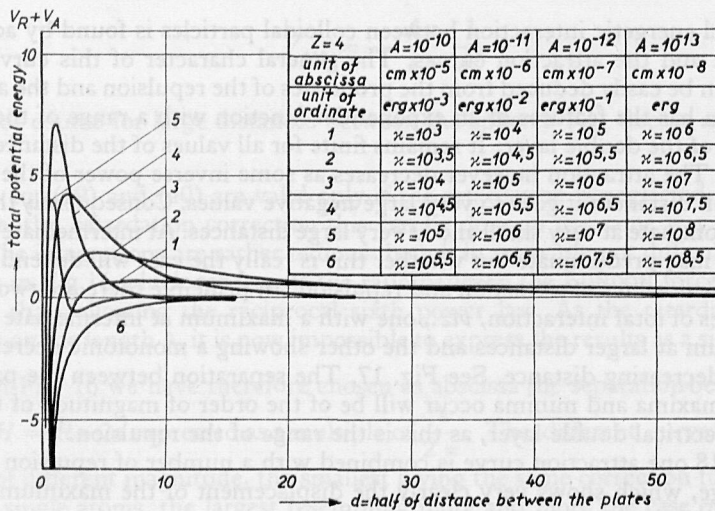 also in the case of more symmetrically formed crystal-line particles we may expect that the description of flat plates will give us information on the behaviour of the system. Indeed the interaction of, say, cubical particles which approach each other with sides of the cubes facing each other, will be well described



Fig. 17. Combination of one attraction curve with two repulsion curves of different height.



| Z=4 | $A=10^{-10}$ | $A=10^{-11}$ | $A=10^{-12}$ | $A=10^{-13}$ |
|---|---|---|---|---|
| unit of abscissa | $cm \times 10^{-5}$ | $cm \times 10^{-6}$ | $cm \times 10^{-7}$ | $cm \times 10^{-8}$ |
| unit of ordinate | $erg \times 10^{-3}$ | $erg \times 10^{-2}$ | $erg \times 10^{-1}$ | $erg$ |
| 1 | $\varkappa=10^{3}$ | $\varkappa=10^{4}$ | $\varkappa=10^{5}$ | $\varkappa=10^{6}$ |
| 2 | $\varkappa=10^{3,5}$ | $\varkappa=10^{4,5}$ | $\varkappa=10^{5,5}$ | $\varkappa=10^{6,5}$ |
| 3 | $\varkappa=10^{4}$ | $\varkappa=10^{5}$ | $\varkappa=10^{6}$ | $\varkappa=10^{7}$ |
| 4 | $\varkappa=10^{4,5}$ | $\varkappa=10^{5,5}$ | $\varkappa=10^{6,5}$ | $\varkappa=10^{7,5}$ |
| 5 | $\varkappa=10^{5}$ | $\varkappa=10^{6}$ | $\varkappa=10^{7}$ | $\varkappa=10^{8}$ |
| 6 | $\varkappa=10^{5,5}$ | $\varkappa=10^{6,5}$ | $\varkappa=10^{7,5}$ | $\varkappa=10^{8,5}$ |

Fig. 18. Illustrating the influence of the concentration of electrolyte (expressed through $\varkappa$: cf. inserted table) on the potential energy curve.

as flat plates when the distance between the cubes is small compared with their linear dimensions.

Moreover it will be shown in chapter VIII that the general properties of lyophobic stability can be derived from the interaction of flat plates.

A great number of variables influence the interaction of flat plates. The concentration and the valency of the electrolytes are important but so, too, are the potential of the surface and the value of the LONDON constant. In § 3b we have already seen that many possible interaction curves can be easily transformed into each other by a suitable choice of the units of energy and distance.

For a given value of $Z$ ($\frac{ze}{kT}$ times the potential of the surface) the energy of repulsion is given by

$$V_R = \frac{\varkappa}{z^2} \, f \, (\varkappa \, d)$$

In the same way the energy of attraction, which is proportional to $d^{-2}$, can be given as

$$V_A = \frac{\varkappa}{z^2} \, z^2 \, \varkappa \, A \, g \, (\varkappa \, d)$$

Hence a certain curve of total interaction giving the energy as a function of the distance is also valid for another set of values of $\varkappa$ and $z$ if the unit of energy is changed in the ratio $\frac{\varkappa_2}{z_2^2} \Big/ \frac{\varkappa_1}{z_1^2}$, the value of $A$ in the ratio $z_1^2 \varkappa_1 / z_2^2 \varkappa_2$ and the unit of the length in the ratio $\varkappa_1/\varkappa_2$. A set of typical interaction curves is given in the Figs. 19-23 in which the units of length and energy and the value of $A$ to match it are mentioned in the insets.

In Fig. 19 even for the highest values of the potential of the surface the attraction prevails for all distances. Fig. 20 which as compared to Fig. 19 has lower values of the
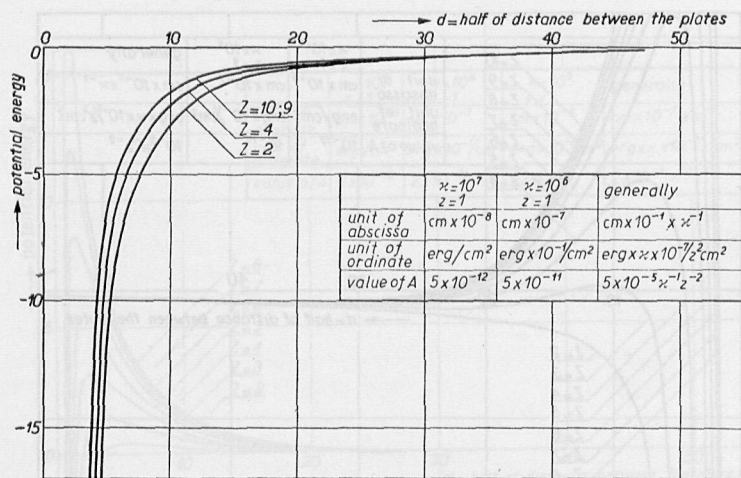


| | $\varkappa = 10^7$ $z = 1$ | $\varkappa = 10^6$ $z = 1$ | generally |
|---|---|---|---|
| unit of abscissa | $cm \times 10^{-8}$ | $cm \times 10^{-7}$ | $cm \times 10^{-1} \times \varkappa^{-1}$ |
| unit of ordinate | $erg/cm^2$ | $erg \times 10^{-1}/cm^2$ | $erg \times \varkappa \times 10^{-7}/z^2 cm^2$ |
| value of A | $5 \times 10^{-12}$ | $5 \times 10^{-11}$ | $5 \times 10^{-5} \varkappa^{-1} z^{-2}$ |

Fig. 19. Curves giving the total potential energy per cm² against the separation of the plates. Potential of the plates $\psi_o = Z \times 25.6$ mV. The electrolyte is supposed to be univalent. For other units *cf.* the conversion tables inserted in the figure.

LONDON constant $A$, shows clearly the transition of curves with a maximum for high values of the potential to curves without a maximum for values of $Z$ equal to 4 or lower. Each of the following figures has been constructed for lower values of the LONDON constant, leading to a continually greater preponderance of the repulsion.

When we realize that stable colloids can only be expected when the potential energy curve shows a maximum and that for univalent electrolytes the flocculation value
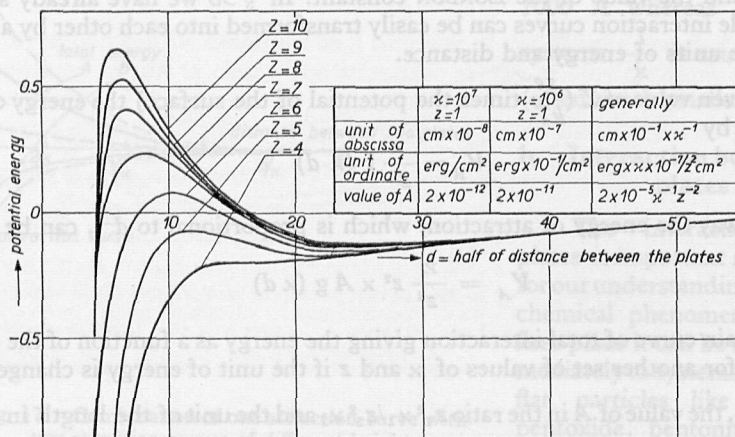


Fig. 20. Curves giving the total potential energy per cm² against the separation of the plates. Potential of the plates $\psi_o = Z \times 25.6$ mV. The electrolyte is supposed to be univalent. For other units *cf*. the conversion tables inserted in the figure.
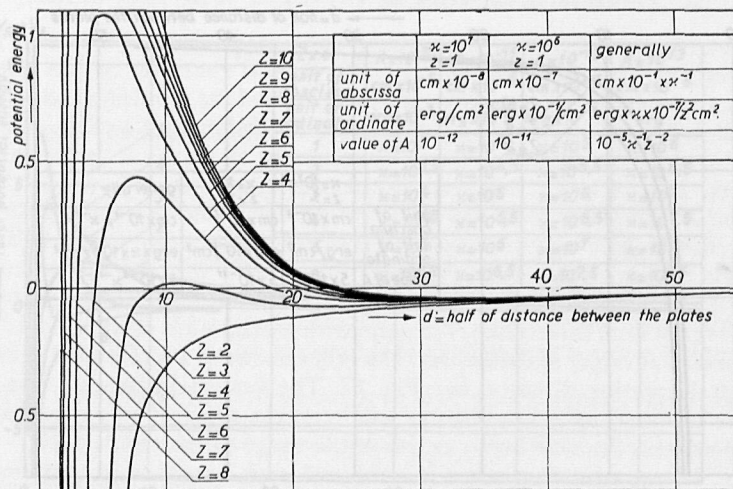


Fig. 21. Curves giving the total potential energy per cm² against the separation of the plates. Potential of the plates $\psi_o = Z \times 25.6$ mV. The electrolyte is supposed to be univalent. For other units *cf*. the conversion tables inserted in the figure.

is usually found to be of the order of 100 m mol/1 ($\varkappa = 10^7$) we see from the Figs. 19-23 that stability for this concentration of electrolytes and not too high potentials, demands a value of $A$ in the neighbourhood of $10^{-12}$ which is in quite good accordance with the theoretical evaluation of $A$ mentioned in § 10a.

A more detailed discussion on colloid stability, in which we shall also make use of the STERN correction, will be given in chapter VIII because a good understanding
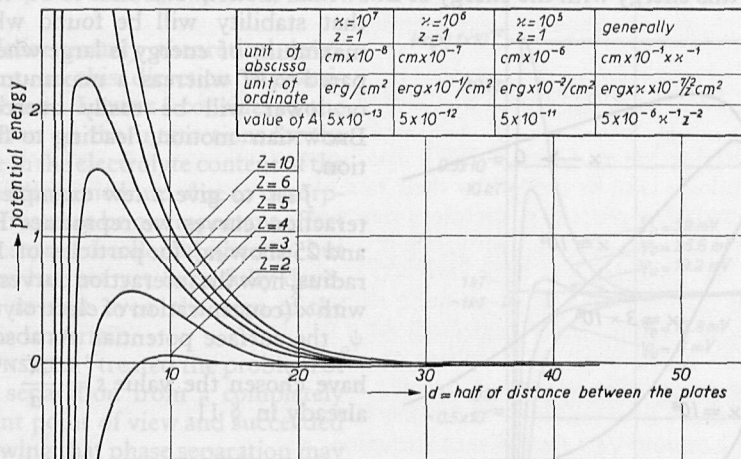


| | $\varkappa = 10^7$<br>$z = 1$ | $\varkappa = 10^6$<br>$z = 1$ | $\varkappa = 10^5$<br>$z = 1$ | generally |
|---|---|---|---|---|
| unit of abscissa | $cm \times 10^{-8}$ | $cm \times 10^{-7}$ | $cm \times 10^{-6}$ | $cm \times 10^{-1} \varkappa \varkappa^{-1}$ |
| unit of ordinate | $erg/cm^2$ | $erg \times 10^{-1}/cm^2$ | $erg \times 10^{-2}/cm^2$ | $erg \varkappa \varkappa \times 10^{-7}/z^2 cm^2$ |
| value of A | $5 \times 10^{-13}$ | $5 \times 10^{-12}$ | $5 \times 10^{-11}$ | $5 \times 10^{-6} \varkappa^{-1} z^{-2}$ |

Fig. 22. Curves giving the total potential energy per $cm^2$ against the separation of the plates. Potential of the plates $\psi_0 = Z \times 25.6$ mV. The electrolyte is supposed to be univalent. For other units *cf.* the conversion tables inserted in the figure.
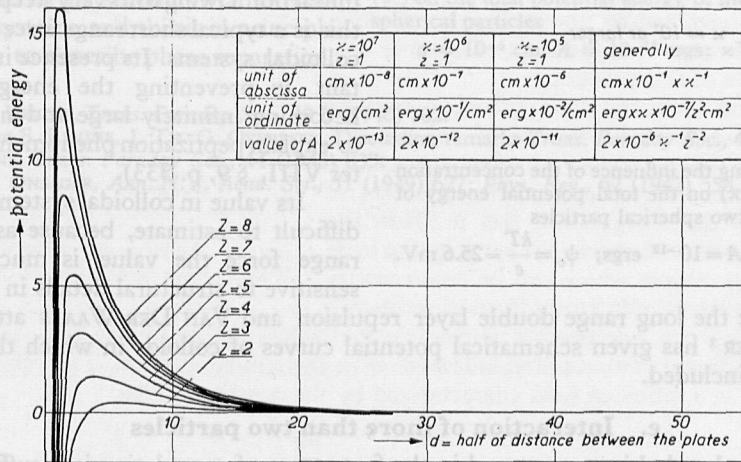


| | $\varkappa = 10^7$<br>$z = 1$ | $\varkappa = 10^6$<br>$z = 1$ | $\varkappa = 10^5$<br>$z = 1$ | generally |
|---|---|---|---|---|
| unit of abscissa | $cm \times 10^{-8}$ | $cm \times 10^{-7}$ | $cm \times 10^{-6}$ | $cm \times 10^{-1} \varkappa \varkappa^{-1}$ |
| unit of ordinate | $erg/cm^2$ | $erg \times 10^{-1}/cm^2$ | $erg \times 10^{-2}/cm^2$ | $erg \varkappa \varkappa \times 10^{-7}/z^2 cm^2$ |
| value of A | $2 \times 10^{-13}$ | $2 \times 10^{-12}$ | $2 \times 10^{-11}$ | $2 \times 10^{-6} \varkappa^{-1} z^{-2}$ |

Fig. 23. Curves giving the total potential energy per $cm^2$ against the separation of the plates. Potential of the plates $\psi_0 = Z \times 25.6$ mV. The electrolyte is supposed to be univalent. For other units *cf.* the conversion tables inserted in the figure.

of stability can only be given after the treatment of the kinetics of flocculation (chapter VII).

## c. Interaction of spherical particles

In the same way as for flat plates the repulsion and attraction curves can be combined for spherical particles to give curves of total interaction.

In this case we express the energy as energy per pair of particles and can immediately compare this energy with the energy of BROWNian motion. It is thus to be expected that stability will be found when the maximum of energy is large when compared to $kT$ whereas a maximum of $kT$ or lower will be easily overcome by BROWNian motion, leading to flocculation.

Just to give a few examples of interaction curves we reproduce Figs. 24 and 25 showing, for particles of $10^{-5}$ cm radius, how the interaction curves change with $\varkappa$ (concentration of electrolytes) and $\psi_{\circ}$ the surface potential. As abscissa we have chosen the value $s = \dfrac{R}{a}$ defined already in § 11.

## d. The Born repulsion

It has been mentioned in § 10a that for very small distances the BORN repulsion between the electronic clouds comes into action. Owing to its very steep descent this is a typical short range force even for colloidal systems. Its presence is important in preventing the energy from becoming infinitely large and in helping to explain peptization phenomena (chapter VIII, § 9, p. 333).

Its value in colloidal systems is very difficult to estimate, because as a short range force the value is much more sensitive to structural details in the surface than are the long range double layer repulsion and VAN DER WAALS attraction.
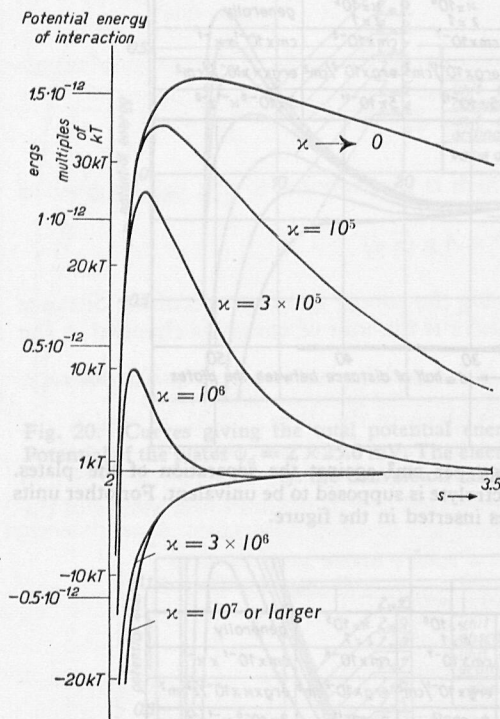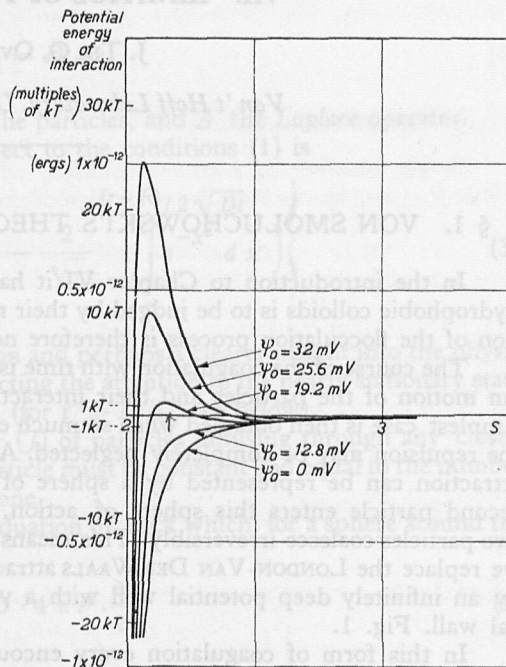


Fig. 24. Showing the influence of the concentration of electrolyte ($\varkappa$) on the total potential energy of interaction of two spherical particles

$a = 10^{-5}$ cm; $A = 10^{-12}$ ergs; $\psi_{\circ} = \dfrac{kT}{e} = 25.6$ mV.

HAMAKER [1] has given schematical potential curves of colloids in which the BORN repulsion is included.

## e. Interaction of more than two particles

In stable lyophobic systems and in the first stages of coagulation it is sufficient to consider only encounters between two particles, as multiple encounters are too rare

[1] H. C. HAMAKER, *Rec. trav. chim.*, 56 (1937) 3.

to have any appreciable influence. In the further course of coagulation when larger agglomerates have been formed, interaction of more than two particles becomes important.

Perhaps still more important is the interaction of many particles in the phase separation found in systems with elongated or flattened particles. (See chapter VIII, § 7, p. 326) [1].

Unfortunately theoretical development in this direction is practically absent. LEVINE [2] considered the correction on the interactions for the change in the electrolyte content of the surrounding medium due to desorption. This may be an important effect in concentrated colloidal systems, but the idea has not yet been fully developed so that even the sign of the effect is uncertain.

ONSAGER [3] treated the problem of phase separation from a completely different point of view and succeeded in showing that phase separation may be due partly to entropy effects. Also in his calculation, however, all interactions are described as interactions by pairs which enables him to find the analogue of the second virial for colloidal systems and this is in principle enough to describe phase separation.



Fig. 25. Showing the influence of the surface potential ($\psi_0$) on the total potential energy of interaction of two spherical particles

$a = 10^{-5}$ cm; $A = 10^{-12}$ ergs; $\varkappa = 10^6$ cm$^{-1}$.

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[1] S. LEVINE, Trans. Faraday Soc., 42 B (1946) 102.

[2] See S. LEVINE, J. TH. G. OVERBEEK, Discussion remarks Trans. Faraday Soc., 42 B (1946) 128; S. LEVINE, Trans. Faraday Soc., 44 (1948) 833.

[3] L. ONSAGER, Ann. N.Y. Acad. Sci., 51 (1949) 627; Phys. Rev., 62 (1942) 558.