Thermodynamic Stabilization of Colloids

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An analysis is given of the conditions necessary for obtaining a thermodynamically stable dispersion (TSD) of solid particles in a continuous aqueous solution phase. The role of the adsorption of potential-determining ions at the planar interface in lowering the interfacial free energy (γ) to promote spontaneous dispersion is stressed. In this respect the importance of the point-of-zero-charge (PZC) and of the point-of-zero-surface tension (PZS) in the quantitative description of the dispersion process are discussed. It is reasoned that for simple inorganic solids a decrease in γ by about 200 mN m^{-1} relative to its value at the PZC may be sufficient to yield a TSD. The equilibrium dispersion will be characterized by a very small but positive γ and a near isodispersity. Suggestions are made for preparing by precipitation dispersions which may prove to be thermodynamically stable. The differences and similarities between these dispersions and the well-known kinetically stabilized sols of lyophobic colloids are briefly enumerated and discussed.

INTRODUCTION

Colloid science may be said to have developed from a desire to understand the observed stability of many colloidal solutions. As these systems bridge the gap between molecular solutions and two-phase macrosystems it has proven convenient at times to treat the colloidal particle as one of the solute components of a solution phase and then again as the disperse phase of a two-phase system. Excellent treatments of the thermodynamics of disperse systems in which this dual description is emphasized have been given by Tolman (1), Hermans (2), and Rusanov *et al.* (3).

It is also important to distinguish between a system which is thermodynamically stable and one which owes its stability to kinetic factors. Until quite recently it was believed that only certain types of colloidal systems may exhibit thermodynamic stability. Thus solutions of lyophilic colloids—macromolecules and association colloids—are known

to be thermodynamically stable over wide ranges of concentration. Dispersions of so-called lyophobic colloids (emulsions and finely divided solids) were considered to be thermodynamically unstable and to owe their observed stability to energetic and/or entropic barriers, the origin of which is largely accounted for by the well-known DLVO theory. It would therefore seem possible to distinguish, solely on the basis of the nature and composition of the dispersed phase, between a thermodynamically stable dispersion (TSD) and a kinetically stable dispersion (KSD). Yet it was realized that both types (TSD and KSD) have many common features. Thus, for example, the same types of forces are invoked to explain the interaction between two soap micelles, two emulsion droplets, or two solid particles in a silver iodide sol.

As early as 1913 Tolman (1) argued that lyophobic colloids should form thermodynamically stable solutions if by adsorption the interfacial tension between the condensed disperse phase (an emulsion droplet or solid particle) and the dispersing liquid medium were to become zero. Tolman's

the interface separating a sparingly soluble salt AB from an aqueous electrolyte solution. Consider the solid AB to be in contact with an aqueous solution to which is also added a potential-determining electrolyte AY and a supporting electrolyte XY. For this two-phase, four-component system at constant temperature and pressure the Gibbs adsorption equation reads

$$d\gamma = -(\Gamma_{A^+} - \Gamma_{B^+})d\mu_{AY} - \Gamma_{X^+}d\mu_{XY}. \quad [2]$$

The relative adsorption density or surface excess of component AY is rigorously defined by the relation

$$(\Gamma_{A^+} - \Gamma_{B^-})$$

$$= -\left(\frac{\partial\gamma}{\partial\mu_{AY}}\right)T, p, \mu_{XY} \quad [3a]$$

$$= \left(\frac{\partial n_{AY}}{\partial A}\right)T, p, n_{H_2O}, n_{AB}, \mu_{AY}, \mu_{XY}. \quad [3b]$$

Equation [3b] serves as an operational definition of the adsorption density in systems where changes in γ are not accessible to measurement, A refers to the total interfacial area, and n_i to the number of moles of component i in the system.

We define the surface charge density σ as the excess adsorption of lattice (potential-determining) ions

$$\sigma \equiv F(\Gamma_{A^+} - \Gamma_{B^-}), \quad [4]$$

where F is the Faraday constant. On introducing the electrochemical potential $\tilde{\mu}_j$ of the ionic species j and making use of Eq. [4], Eq. [2] may be rewritten to yield

$$d\gamma = -\frac{\sigma}{F}d\tilde{\mu}_A - \Gamma_{X^+}d\mu_{XY} - \frac{\sigma}{F}d\tilde{\mu}_Y. \quad [5]$$

At constant ionic strength and $c_{XY} \gg c_{AY}$, Eq. [2] simplifies to

$$d\gamma = -(\Gamma_{A^+} - \Gamma_{B^-})d\mu_{AY} \quad [6]$$

and Eq. [5] becomes

$$d\gamma = -\frac{\sigma}{F}d\tilde{\mu}_A. \quad [7]$$
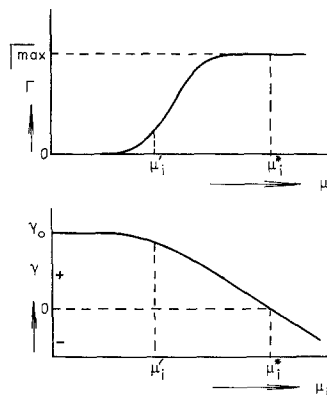
FIG. 1. Illustrating the variation of adsorption density and interfacial tension with chemical potential of adsorbate. μ_i^* is the chemical potential at the point-of-zero-surface tension (PZS) when saturation adsorption is already achieved.

Equation [6] may be integrated to find the decrease in γ at constant ionic strength if the dependence of $(\Gamma_{A^+} - \Gamma_{B^-})$ on μ_{AY} (the adsorption isotherm) is known. Equation [7] will serve as the starting point in a theoretical evaluation of the decrease of the interfacial tension due to adsorption at the plane interface.

On formally separating the electrochemical potential into a chemical and an electrical term and noting that at equilibrium $\tilde{\mu}_i$ must be constant throughout the two-phase system, we may write the following equivalent expressions for $d\tilde{\mu}_A$:

$$d\tilde{\mu}_A = d\tilde{\mu}_A^l = RTd \ln a_A \quad [8a]$$

$$= d\tilde{\mu}_A^b = Fd\phi \quad [8b]$$

$$= d\tilde{\mu}_A^s = d\mu_A^{(c,s)} + Fd\psi_0, \quad [8c]$$

where ϕ is the Galvani potential difference between the two bulk phases, namely, solid (b) and solution (l), and ψ_0 is the average electrostatic potential at the surface (s) relative to that of the bulk solution (l) which is arbitrarily assigned a value of zero. The activity of species A^+ in the solution is represented by a_A and $\mu_A^{(c,s)}$ denotes the chemical part of the electrochemical potential of A in the surface. On substituting expression [8c] for $d\tilde{\mu}_A$ in Eq. [7] we find
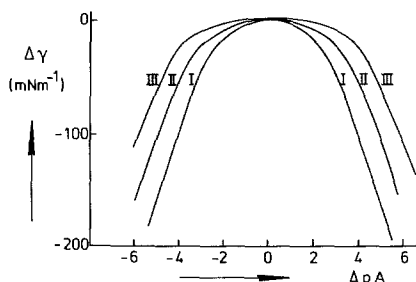
FIG. 2. Calculated curves of $\Delta\gamma$ versus ΔpA. Curve I: Ionic strength 1 M; curve II: ionic strength 0.1 M; curve III: ionic strength 0.01 M. $\sigma_{max} = 1$ C/m^2.

$$dy = -\sigma d\psi_0 - \frac{\sigma}{F} d\mu_A^{(c,s)}. \qquad [9]$$

This quasi-thermodynamic relation defines an electrical and a chemical contribution to the lowering of the interfacial tension. To evaluate the chemical contribution we shall assume localized reversible adsorption of the ions at noninteracting surface sites. Based on this simple Langmuir adsorption model we write (9)

$$d\mu^{(c,s)} = RTd \ln \frac{\theta}{1 - \theta} \qquad [10]$$

where θ is the fraction of the total number of sites occupied by ion A$^+$ at the solid/liquid interface. We distinguish two types of sites, one for occupation by A$^+$ and the other for occupation by B$^-$. It may then be shown (5) that

$$\theta = \frac{(\sigma_{max} + \sigma)}{2\sigma_{max}}, \qquad [11]$$

where $\sigma_{max} = 2F\Gamma_{PZC}$ and Γ_{PZC} is the adsorption density at the point of zero charge when $\sigma = 0$ and Γ_{A^+} and Γ_{B^-} both equal $\frac{1}{2}\Gamma_{max}$. On choosing a suitable model for the electrical double layer the dependence of σ on ψ_0 may be found and the evaluation of the electrical contribution to the interfacial tension lowering can be made. Note that according to Eqs. [8a] and [8c] the magnitude of the potential difference ψ_0 is fixed once an expression for $\mu^{(c,s)}$ is formulated. On substituting into Eq. [9] the defining ex-

pressions [10] and [11] for $\mu^{(c,s)}$ and θ and applying the Guoy–Chapman theory of the electrical double layer to find a relation between σ and ψ_0 (10), we find after integration

$$\Delta\gamma = \gamma - \gamma_0$$

$$= -\frac{8cRT}{\kappa} \left[\cosh \frac{F\psi_0}{2RT} - 1 \right]$$

$$+ \frac{RT}{F} \sigma_{max} \ln \left(1 - \frac{\sigma^2}{\sigma_{max}^2} \right), \quad [12]$$

where c is the total electrolyte concentration, γ_0 is the value of the interfacial tension at the PZC, and κ is the reciprocal Debye length. We note that both terms on the right-hand side of the above equation contribute to a decrease in γ.

By introducing an alternative expression for the "double layer" term, Eq. [12] may be rewritten

$$\Delta\gamma = \frac{2RT}{F} (\sigma_- - \sigma_+)$$

$$+ \frac{RT}{F} \sigma_{max} \ln \left(1 - \frac{\sigma^2}{\sigma_{max}^2} \right), \quad [13]$$

where $\sigma_-(\sigma_+)$ is the charge density of the anions (cations) in the diffuse part of the double layer. The above result may be compared with a similar calculation by Hachisu (11) for ionized monolayers at liquid–liquid interfaces. It should, however, be noted that the adsorbing ions in the monolayer are assumed perfectly mobile in the Hachisu model.

To relate our theoretical evaluation of $\Delta\gamma$ to experimental measurements we give in Fig. 2 a plot of $\Delta\gamma$ versus ΔpA as derived from Eq. [12]. The parameter ΔpA equals the difference pA $-$ pA$_0$ where the subscript o refers to the PZC of the system.

With reference to Eqs. [12] and [13] we note that at low surface coverages, thus also low ΔpA values, the electrical term makes the major contribution to the value of $\Delta\gamma$. When the surface is nearly saturated ($\sigma \simeq \sigma_{max}$), the "chemical" term provides the

major contribution. Under these conditions (near adsorption saturation) ψ_0 will be approximately constant and according to Eqs. [8] and [9] a linear dependence of $\Delta\gamma$ on ΔpA or $\Delta\mu$ will result. This situation was anticipated when writing Eq. [1].

The linear dependence of $\Delta\gamma$ on ΔpA at large ΔpA values is evident from Fig. 2. The symmetrical shape of the curves is inherent in the choice of adsorption model. This figure demonstrates that for large values of σ_{max} the decrease in the interfacial tension may amount to as much as a few hundred millinewtons per meter over a ΔpA range of about 6 to 7.

Experimental evaluations of $\Delta\gamma$ may be done with the aid of Eq. [6] and the adsorption isotherm (σ versus pA) obtained with the potentiometric titration technique (12, 13). Adsorption studies with silver iodide as adsorbent indicate that at high ionic strength a negative surface charge density of only about 6×10^{-2} C m^{-2} (13) for $\Delta pAg \simeq 6$. From this low value for σ a decrease in the interfacial tension of the AgI/solution interface of about 15 mN m^{-1} is derived. For oxides σ may reach values an order of magnitude larger than those measured on AgI (14, 15). Obviously for these systems a more pronounced decrease in the interfacial tension will result. Values in the neighborhood of 150 mN m^{-1} have been quoted (16).

In arriving at the $\Delta\gamma$–ΔpA curves displayed in Fig. 2 we have chosen model parameters (for example, σ_{max}) so as to obtain over the same ΔpA range a decrease in the interfacial tension of the same order of magnitude as that observed in oxide systems. Our calculations show that a combination of high ionic strength, a large ΔpA value, and a high σ_{max} favors a strong reduction in the interfacial tension. The decrease in the interfacial tension ($\Delta\gamma$) needed to make γ negative and promote spontaneous dispersion will depend on the value of γ_0. Unfortunately no reliable experimental technique is available for measuring the interfacial tension of solids in aqueous solutions. Experimental

studies of the kinetics of precipitation from supersaturated aqueous solutions (17) and elementary calculations (18) suggest that for simple, sparingly soluble salts and some simple oxides γ values ranging from 50 to 300 mN m^{-1} are to be expected. One may therefore expect to find experimental proof of the existence of TSD of these solids. It is also interesting to note that if the thermodynamic stability of a dispersion has been demonstrated then a more exact value than hitherto possible may be deduced for the interfacial tension of a solid in aqueous solution.

FORMATION OF THERMODYNAMICALLY STABLE DISPERSIONS

The thermodynamic conditions which determine the existence of stable and unstable equilibrium disperse systems and spontaneously dispersing systems may be derived straightforwardly from a formulation of the free energy of formation (ΔG) of a dispersion of arbitrary size. A number of investigators (19–22) have used this approach in an analysis of the stability of microemulsions. A most elegant treatment applicable to all types of disperse systems has been given by Rusanov et al. (3, 23). A number of these authors introduced statistical thermodynamical considerations to correct for deviations from ideal behavior of the colloidal solutions and thus to account for the interaction between dispersed particles. Overbeek's treatment (20) is the most advanced. He introduces the Percus–Yevick–Carnahan–Starling approximation (24) for hard spheres to correct for nonideal behavior and estimates the magnitude of this correction. This author also considers the effect of curvature on the decrease in the interfacial tension in both W/O and O/W microemulsions.

General Formulation of the Condition for Stable Equilibrium of Solid Dispersions

We do not intend to give a detailed and rigorous treatment of the conditions for

stable equilibrium of solid dispersions in aqueous solution. In the preceding section the role of adsorption in promoting spontaneous dispersion has been discussed. We merely wish now to arrive at an order of magnitude approximation of the degree of dispersion of the equilibrium system. Consider the formation of a dispersion by subdivision of a (macro)solid phase AB in an aqueous solution of fixed composition to yield spherical particles of radius r. At constant temperature, pressure, and composition we may write for the free energy of formation of this dispersion

$$\Delta G_{T,p,\text{ all } n's}$$

$$= \gamma A + \sum n_i \Delta \mu_i + \Delta G_{\text{mix}}. \quad [14]$$

The first term on the right-hand side of Eq. [14] represents the amount of reversible work to increase the surface area of the system from an assumed negligible value in the initial state to its final value A. It will make a positive contribution if γ is positive and a negative contribution for γ negative. The second term, referred to by Ruckenstein (21) as the "dilution effect" will be negative because of adsorption at the newly created interface or zero in the absence of adsorption. The last term represents the free energy of mixing of the dispersed particles into the continuous medium and makes a negative contribution because entropy is generated in the process. This term may be evaluated by assuming the formation of a dilute dispersion of n_p noninteracting particles. In this case we may write

$$\Delta G_{\text{mix}} = -kTn_p\{\ln (N/n_p) + 1\}, \quad [15]$$

where k is the Boltzmann constant and $N \gg n_p$ is the number of solvent molecules in the system. This formulation corresponds to that derived by Rehbinder and Shchukin (25). For a dispersion of spherical particles of radius r we may also write

$$\gamma A = \gamma B n_p^{1/3}, \quad [16]$$

where

$$B = (36 n_{AB}^2 \bar{v}^2 \pi)^{1/3} \quad [17a]$$

and we have made use of the identities

$$n_p = \frac{3\bar{v}n_{AB}}{4\pi r^3} = (36\pi n_{AB}^2 \bar{v}^2)^{-1}A^3 \quad [17b]$$

$$A = \frac{3\bar{v}n_{AB}}{r}. \quad [17c]$$

In these expressions n_{AB} is the number of moles of the solid AB to be dispersed, $\bar{v}$ is the molar volume, and A is the total surface area of the dispersed phase. Note that parameter B is a constant if the change in solubility of the solid with variation in particle size may be ignored.

On applying the condition for thermodynamic equilibrium to Eq. [14] after having made the substitutions indicated by Eqs. [15] and [16] and recalling the Gibbs–Duhem relation, we find

$$\frac{\partial \Delta G}{\partial n_p} = 0$$

$$= \frac{1}{3}Bn_p^{-2/3}\gamma - kT \ln N/n_p. \quad [18]$$

From Eq. [18] we conclude that the interfacial tension of the equilibrium dispersion must be *positive* irrespective of the particular expression used to evaluate ΔG_{mix}. Solving for the equilibrium value of the interfacial tension (γ_e), we obtain

$$\gamma_e = \frac{3kT}{4\pi r_e^2} \ln \frac{N}{n_p}. \quad [19]$$

In the Appendix we list some values for γ_e as calculated with the aid of this expression.

The condition for a stable equilibrium, $\partial^2 \Delta G/\partial^2 n_p > 0$, when applied to this ideal dilute dispersion requires

$$-\frac{2}{9}B\gamma n_p^{-5/3} + \frac{1}{3}Bn_p^{-2/3}$$

$$\times \left(\frac{\partial \gamma}{\partial n_p}\right) + kTn_p^{-1} > 0. \quad [20]$$

Whether the equilibrium will be a stable one or not will depend largely on the sign of the partial derivative $\partial \gamma/\partial n_p$ which will be discussed later.

THERMODYNAMIC STABILIZATION OF COLLOIDS

Estimating the Particle Size of the Thermodynamically Stable Dispersion

The condition for equilibrium, Eq. [18], does not allow one to solve explicitly the concentration (and particle size) of the equilibrium dispersion unless γ_e is known. A reasonable estimate of the particle size may be obtained by considering the role of adsorption in the dispersion process at constant T, p, and composition. The total number of adsorbed potential-determining ions at the spherical interface (total area A) is

$$n_{A^+}^S - n_{B^-}^S = \frac{\sigma A}{F} = \frac{\sigma}{F}\left(\frac{3n_{AB}\bar{v}}{r}\right). \quad [21]$$

A materials balance shows that

$$c_{AY} = \frac{3n_{AB}\bar{v}\sigma}{VF}\left(\frac{1}{r}\right) + (c_A - c_B), \quad [22]$$

where c_{AY} is the number of moles of the potential-determining electrolyte initially added per unit volume of liquid phase, the concentration difference $(c_A - c_B)$ refers to the excess concentration of A^+ in the solution when adsorption equilibrium is reached, and V is the volume of the continuous phase which may be assumed constant. For c_{AY} large and therefore $c_A \gg c_B$ Eq. [22] transforms to

$$c_{AY} - c_A = \frac{3n_{AB}\bar{v}\sigma}{VF}\left(\frac{1}{r}\right). \quad [23]$$

With the aid of this expression and the previously derived relation between $\Delta\gamma$ and ΔpA (see Eq. [12], also Fig. 2) it is now possible to evaluate the change in interfacial tension with variation in r during the dispersion process for a fixed value of c_{AY}. The results of this calculation are displayed in Fig. 3 where we plotted $\Delta\gamma$ versus $\log r$ at three different ionic strengths but at the same predetermined value of c_{AY}. The dashed line in this figure locates the zero value of γ on the assumption that γ_0 equals 150 mN m^{-1}. We note that the macrosystem
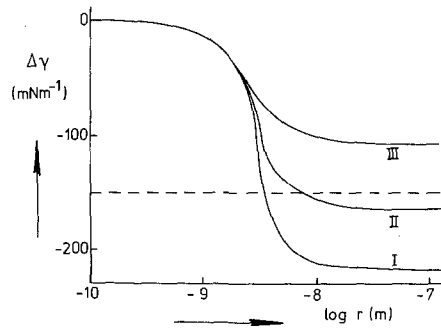
FIG. 3. Calculated curves depicting variation of $\Delta\gamma$ with $\log r$ with r = average radius of the dispersed phase. Curve I: Ionic strength 1 M; curve II: ionic strength 0.1 M; curve III: ionic strength 0.01 M. $\sigma_{max} = 1$ C m^{-2}; $n_{AB} = 1$ mole; $V = 1$ dm^3; pA (at PZC) = 6; $\bar{v} = 10^{-5}$ m^3/mole; $c_{AY} = 0.1$ M.

at ionic strength 1 M and 0.1 M will be unstable $(\gamma < 0)$ under these conditions. In fact negative γ values will be observed for $r > 10^{-8.5}$ m (ionic strength 1 M) and for $r > 10^{-8.1}$ m (ionic strength 0.1 M). Spontaneous dispersion will occur. Stable equilibrium dispersions characterized by an average particle size approximately 3 nm $(I = 1 M)$ and 8 nm $(I = 0.1 M)$ will thus form.

If, however, $\gamma_0 \geqslant 250$ mN m^{-1} all dispersions regardless of ionic strength will be unstable. The stable state will be the two-phase macrosystem characterized by a minimal surface area.

At the point-of-zero-surface tension where $\gamma = 0 (|\Delta\gamma| = \gamma_0)$ and pA $\equiv$ pA* we derive from Eq. [23] (see also Figs. 1 and 2)

$$c_{AY} - c_A^* = \frac{\text{constant}}{r^*}\sigma_{max}. \quad [24]$$

This useful relation shows that r^* is inversely proportional to the difference $(c_{AY} - c_A^*)$. The larger this difference the smaller r^* will be. Spontaneous dispersion occurs for $c_{AY} > c_A^*$ (or $\Delta pA > \Delta pA^*$) because then the interfacial tension at a planar interface $(r \to \infty)$ will be negative. The equilibrium size of the dispersion may now be approximated by Eq. [24]. However, because at equilibrium γ must be positive, the

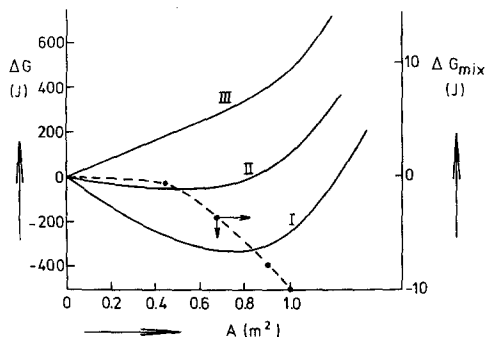FIG. 4. The variation of the free energy of formation (ΔG) of a dispersion with total surface area (A) at different ionic strengths. The dashed curve gives the contribution of the free energy of mixing to ΔG. For further details see text.

equilibrium radius r_e will always be slightly smaller than r^* (see Fig. 3).

In Fig. 4 we give a plot of ΔG as a function of total surface area. In calculating ΔG we have assumed the same values for c_{AY}, γ_0, and σ_{max} as were chosen for the construction of Fig. 3. From Fig. 4 we see that the minima in the two curves I and II locate the thermodynamically stable dispersions. We also note that the contribution of the ΔG_{mix} term to the total free energy of formation is small compared to the other contributions (dashed curve).

Testing the Condition for Stable Equilibrium

To demonstrate the existence of thermodynamically stable sols we must establish as mentioned previously that $\partial^2 \Delta G / \partial^2 n_p > 0$. We consider two cases. First, we shall assume the two-phase macrosystem to have a low but positive interfacial tension and that no adsorption occurs during the dispersion process. In the second case we consider systems in which a significant role is played by adsorption in the dispersion process.

The increase in free energy accompanying the increase in surface area in case I will be compensated entirely by the ΔG_{mix} term. If a stable dispersion were to form then ac-

cording to Eq. [20] the condition to be satisfied is

$$- \frac{2}{3} \frac{kT}{n_p} \ln \frac{N}{n_p} + \frac{kT}{n_p} > 0. \qquad [25]$$

Now for dilute solutions to which the above criterion applies, the negative term on the left-hand side will be much larger numerically than the positive entropic term. Only for $N/n_p < 4.5$ will the criterion for stability be obeyed but then ideal behavior may no longer be assumed. We conclude therefore that for this case the condition for stable equilibrium is not met. This conclusion is not surprising. According to Eq. [18] the equilibrium radius will be quite large for a low equilibrium value of the interfacial system (see Appendix). An additional decrease in particle radius will result in a large gain in entropy (approximately proportional to r^{-3}) for a small decrease in the free energy of surface formation (proportional to r^{-1}). The existence of an "entropy stabilized" sol is therefore not to be expected. It is possible that dispersions of some organic solids in nonpolar liquids may belong to this category.

In case II the partial derivative $\partial \gamma / \partial n_p$ is not zero. We must introduce an adsorption model to evaluate the derivative as was done by Wagner (19) for a microemulsion system. The last term in Eq. [20] may be neglected because as already pointed out the first term is much larger numerically than it. The condition for stable equilibrium then becomes

$$\frac{\partial \gamma}{\partial n_p} > \frac{2}{3} \frac{\gamma}{n_p} \qquad [26a]$$

or

$$\frac{3}{2} n_p \frac{\partial \gamma}{\partial n_p} > \gamma. \qquad [26b]$$

The term on the left-hand side of these inequalities can be evaluated with the aid of the adsorption model introduced in previous sections of this paper. Starting with the Gibbs adsorption equation in the form $-d\gamma$

$= (RT\Gamma_{A+}/c_A)dc_A$ and utilizing Eqs. [17b] and [24] it is readily shown that

$$\frac{\partial \gamma}{\partial n_p} = \frac{RT\Gamma_{max}^2}{c_A^* V} \cdot \frac{4\pi r^{*2}}{3} . \quad [27]$$

To test the stability criterion, Eq. [26], we show calculations of the term

$$\frac{3}{2} n_p \frac{\partial \gamma}{\partial n_p} = \frac{3n_{AB}\bar{v}\Gamma_{max}^2 RT}{c_A^* V} \cdot \frac{1}{r^*} \quad [28]$$

for appropriate values of the relevant physical parameters $(n_{AB}, c_A^*, \Gamma_{max})$ in the Appendix. We note that under these conditions $\partial \gamma/\partial n_p$ is larger than the quotient γ/n_p.

The Isodispersity of a TSD

In performing the preceding thermodynamic analysis and in constructing Figs. 3 and 4 we have tacitly neglected the dependence of the solubility of the dispersed phase and of the interfacial tension on the particle size (or its curvature). Starting with the definition of the chemical potential of a one-component phase, $\mu = (\partial G/\partial n)_{T,p}$, an expression may be obtained for the change in solubility with particle size. Thus for an isotropic solid of finite dimensions we may write

$$\mu = \mu_\theta + \gamma(\partial A/\partial n). \quad [29]$$

On introducing the identity $\partial A/\partial n = \bar{v}\partial A/\partial V$ and assuming spherical geometry for the dispersed phase we find

$$\mu - \mu_\theta = \frac{2\gamma\bar{v}}{r} , \quad [30]$$

where μ_θ is the chemical potential of an infinitely large solid. This expression reduces to the well-known Gibbs–Kelvin equation if we assume both γ and $\bar{v}$ to be independent of r. The value to be inserted for γ in Eq. [30] is then that of a plane interface separating the solid and liquid phases at a given temperature and composition. From the above expression we conclude that when γ is small, as would be true for a thermo-

dynamically stable dispersion, the correction to be applied because of the solubility effect may be negligibly small.

The dependence of γ on r (or curvature) is also expected to provide only a second-order correction to the solubility as calculated from the Gibbs–Kelvin equation. Tolman (26) and Kirkwood and Buff (27) calculated that the surface tension of a liquid droplet should decrease with decreasing r but concluded that this effect would be detectable only if the radius of the droplet is smaller than 10 nm and will become appreciable for $r < 1$ nm. Recent investigations by Ahn et al. (28) and by Kim and Chang (29) confirm these conclusions. Whether the same trend (decreasing γ with decreasing r) holds for solid particles has not yet been established with any degree of certainty. There are indications of a similar trend to be expected (30) but also of an opposite behavior (31). Regardless of the direction in which γ will vary with particle size, this effect will only become of importance when the size of the dispersed particles approaches molecular dimensions. A statistical mechanical treatment of the system is then to be preferred to a thermodynamic description of such small-particle systems.

In deriving the Gibbs–Kelvin equation we have also ignored a third effect, namely, the thermal motion of the dispersed particles. From a statistical mechanical analysis Kuhrt (32) was able to show that the translational and rotational motions of small liquid droplets in a continuous vapor add a term, $-4/\nu$, where ν is the number of molecules in a droplet, to the Gibbs–Kelvin equation when written in the form

$$\ln \frac{c(r)}{c(r = \infty)} = \frac{2\bar{v}\gamma}{rRT} . \quad [31]$$

The rotation of solid particles in a liquid medium will probably be greatly hindered so that the correction term may amount at the most to $-3/2 \nu$. Again this effect will only become noticeable when the dispersed phase is

extremely small. It might be important when one treats, for example, a polynuclear metal–hydroxocomplex as a second phase (5).

Although one may justify the neglect of the solubility effect in the derivation of the criteria for stable equilibrium of solid dispersions, it does play an important role when we come to consider the degree of dispersity of the TSD. It is the Gibbs–Kelvin equation that accounts for Ostwald ripening processes in dispersions with positive interfacial tension. A narrow size distribution of the dispersed phase in the TSD is to be expected because of two opposing effects, one of which is Ostwald ripening. The natural tendency for small particles with positive γ to grow larger, as expressed by the Gibbs–Kelvin equation, will be opposed by the so-called adsorption effect which will limit the growth by imposing a negative γ on the larger particles in the dispersion. With reference to Fig. 3 we may then conclude that the steeper the slope ($\partial\gamma/\partial r$ or $\partial\gamma/\partial n_D$) at the point-of-zero-surface tension, the narrower the size distribution and therefore the more nearly isodisperse will be the TSD. The size distribution of equilibrium dispersions in liquid/liquid systems has been considered by Volmer (32) and in more detail by Overbeek (20) for microemulsions. The latter author also concluded that a thermodynamically stable emulsion should be near isodisperse.

DISCUSSION

We have seen that the formation of a thermodynamically stable dispersion of solid particles in a liquid medium is possible if by adsorption at the planar interface a significant lowering of the interfacial tension is achieved such that $|\Delta\gamma| \geq \gamma_0$. The smaller the interfacial tension at the PZC (γ_0) the greater the likelihood that by adsorption spontaneous adsorption would occur. A low γ_0 value is however not an absolute necessity. In systems characterized by a large γ_0 value the required decrease in γ to promote

the formation of a TSD may be achieved by a combined, cooperative adsorption of a potential-determining and another surface-active electrolyte. The observed spontaneous emulsification in some mercury–aqueous solution systems at an applied potential difference of about 1 V (33) may be cited as an example. An asymmetric location of the PZC in the case of simple inorganic solids will also favor the formation of a stable positively or negatively charged sol.

Aside from the small but positive value of the interfacial tension stable dispersions may also be recognized by the absence of marked Ostwald ripening and by a relatively simple relation between the average particle size and the amount of adsorbate needed to create the stable state (see Eq. [24]).

The observations made by Voet (34) in a study of colloidal sols in concentrated electrolyte solutions suggest that he may have been dealing with TSD. This investigator noted, for example, an improved stability of slightly soluble salts and also metal sols in concentrated solutions of sulfuric acid. A positively charged silver iodide sol in a concentrated electrolyte solution was observed to have a greater stability than the corresponding sol in a dilute aqueous solution. Yates (35) observed the remarkable stability of silica sols at high pH and suggested that this might imply thermodynamic stabilization. This observation is in general agreement with the earlier statement that an asymmetric location of the PZC (for silica pH (PZC) $\simeq$ 2) should aid the formation of a TSD. In our investigations of the preparation of aqueous dispersions of Al(OH)$_3$ and FeOOH from acidified metal/salt solutions (5, 36) we also noted at low pH the formation of small particles ($r \simeq 2.5$ nm) which show no tendency for Ostwald ripening. With increasing pH these sols first gelled and then flocculated.

As reverse Ostwald ripening (spontaneous increase in the degree of dispersion) may be kinetically unfavorable we should look for examples of TSD in precipitation studies.

Consider, for example, a hypothetical dispersion of a solid AB in an aqueous solution saturated with respect to the solid phase. Suppose the PZC of the dispersed phase to be located at pA $= 5$ and that due to ionic adsorption the PZS falls at pA $= 2.5$. In Fig. 5 we distinguish three types of systems depending on the excess concentration of the potential-determining electrolyte AY. Dispersions of type A fall in the concentration range $2.5 < pA < 5$ and will through the agency of Ostwald ripening strive to attain a minimum of surface area. Unlimited growth of the solid phase is possible, but kinetically stabilized colloidal dispersions may form. Dispersions of type B represent thermodynamically stable sols of a specified degree of dispersion. The dependence of particle radius on pA as determined by Eq. [24] is also depicted in this figure for type B systems. The lower concentration limit for TSD has been fixed quite arbitrarily by choosing a value of 1 nm for the minimum particle size. Systems of type C are then best considered to be homogeneous solutions (not two-phase systems) but may include as possible components the charged, small polynuclear complexes extensively referred to in solution chemistry.

In the extensive studies by Tezak and co-workers (37) of the precipitation of poorly soluble salts from aqueous solutions examples of TSD may be uncovered. In a typical experiment performed by these investigators two solutions containing soluble salts AY and XB are mixed in various ratios to form the insoluble component AB and electrolyte XY. By turbidity measurements the boundary between a dispersed system and a clear solution is delineated. The results are presented in so-called precipitation diagrams where log [AY] is plotted versus log [XB] and regions in which precipitation is observed are indicated ("precipitation bodies").

Based on the theoretical treatment developed by us we indicate schematically in Fig. 6 the construction of a precipitation diagram.
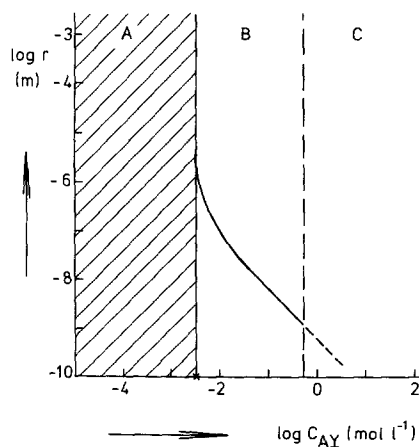

FIG. 5. Illustrating the different types of systems to be encountered in precipitation studies. For details see text. (A) Kinetic stabilization of dispersion is possible but not thermodynamic stabilization. (B) Thermodynamically stable dispersions may exist. The dependence of the equilibrium particle size of the equilibrium composition is depicted by the solid curve (see Eq. [24]). (C) Molecular solutions with as possible components polynuclear complexes exist in this concentration region.

If the interfacial tension of solid AB is positive irrespective of the value of ΔpA or ΔpB then growth and Ostwald ripening will not be restricted. The boundary between precipitation and "dissolution" will be determined by the solubility product. The result is a simple precipitation diagram as sketched in Fig. 6a. We now consider the hypothetical system already referred to for which pA (PZC) $= 5$ and pA* $= 2.5$ (points Q and Q' in Fig. 6b). Between Q and Q' unlimited growth is possible whereas outside this region Eq. [24] will be applicable and small charged particles of AB will form. In Fig. 6b the ruled area includes the dispersions of type A described in Fig. 5 whereas in the blank area labeled "clear" TSD should form. The boundary between these two areas is determined by the condition $c_{AY} = c_A^*$ or $c_{XB} = c_B^*$. The turbidity of the systems falling in the "clear" areas will be low as the concentration of the stable sol will be small. The "clear" areas should merge into the "dissolution" regions which represent simple mo-
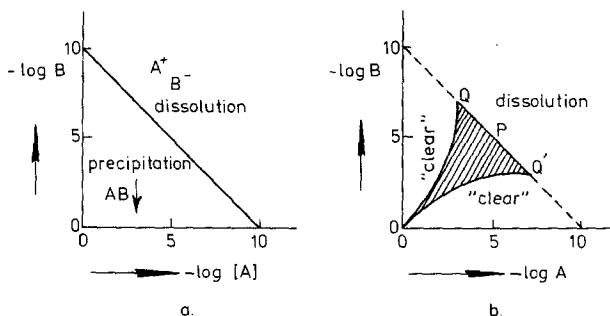
FIG. 6. Illustrating the construction of a precipitation diagram. For details see text. (a) Absence of TSD; (b) TSD possible in region marked "clear."

lecular solutions. It is possible to detect a similarity between our construction (Fig. 6b) and many of the precipitation diagrams of Tezak (37).

In concluding this discussion we wish to compare a kinetically stabilized dispersion (KSD) of which the stability is well accounted for by the DLVO theory to our TSD. A KSD is thermodynamically unstable compared to the two-phase macrosystem which features a minimum of surface area. Spontaneous coarsening of such a dispersion may be hindered kinetically by a high (repulsive) energy barrier to flocculation and/or the very low solubility of the dispersed phase. The van der Waals attraction will, however, eventually overcome the double-layer repulsion when the interacting particles come close together. The system will then find itself in a deep primary energy minimum from which it cannot escape into the dispersed state again.

In the DLVO treatment of colloid stability it is tacitly assumed that the interfacial tension is positive throughout the coagulation process. Once the aggregates of particles of an initially KSD have formed by flocculation irreversible aging processes such as cementing of the particles by recrystallization and Ostwald ripening will take over. Depending on the rates with which these processes proceed the primary particles originally undergoing Brownian motion will have lost their individuality as pointed out by Frens (38). This author also argued and supplied experimental proof that it is possible to reestablish

the double layer by recharging the "precipitated" flocs and thereby to promote redispersion of flocculated systems. However, he was careful to note that redispersion by recharging cannot break up recrystallized and aged aggregates. This is in contrast to a thermodynamically stable dispersion where in principle this reverse Ostwald ripening or comminution process should be thermodynamically feasible but may be hindered by a huge activation barrier.

Obviously the same interaction forces which are invoked in the DLVO treatment of KSD are also operative in TSD. Thus, for example, microemulsions are known to cream, a process similar to that of flocculation of a solid dispersion, but the creamed particles will not coalesce as would be the case in a thermodynamically unstable emulsion. This observation implies that a TSD may be in a sense kinetically unstable. The potential energy diagram of two interacting particles in a TSD may exhibit a reversible secondary minimum and thus show some form of kinetic instability. A clustering of particles may be expected in a concentrated salt solution but were the system to maintain its thermodynamic stability at closer distances repulsive interactions must prevail over attractive actions. Actual contacts between particles are prevented because otherwise the system will land irreversibly in the primary minimum. It might even be possible to consider some of the oxide–gel systems to be immobilized TSD.

APPENDIX

Estimates of the equilibrium interfacial tension (γ_e) and $(3/2)n_p(\partial\gamma/\partial n_p)$ from Eqs. [19] and [28], based on the following reasonable values of the needed physical parameters:

$T = 300°K$, $\bar{v} = 3 \times 10^{-4}$ m³/mole, $n_{AB} = 10^3$ mole/m³, $N = 3.4 \times 10^{28}$ molecules/m³, $c_A = 1$ mole/m³, $V = 1$ m³, $\Gamma_{max} = 1.7 \times 10^{-6}$ mole/m² (16 μC/cm²).

Equilibrium radius (Å)	γ_e (mN m^{-1})	$\dfrac{3}{2}n_p\dfrac{\partial\gamma}{\partial n_p}$ (mN m^{-1})
5	18.4	13,000
10	6.7	6,500
100	0.13	650
1000	0.002	65

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