

Flotation and the Gibbs Adsorption Equation

by P. L. de Bruyn, J. Th. G. Overbeek, and R. Schuhmann, Jr.

THE technique of concentrating valuable minerals from lean ores by flotation depends upon the creation of a finite contact angle at the three-phase contact, mineral-water-air. If the mineral is completely wetted by the water phase, contact angle zero, there is no tendency for air bubbles to attach themselves to the mineral. However, when the contact angle is finite, the surface free energy of the system, water-air bubble-mineral particle, can be diminished by contact between the bubble and the particle, and if not too heavy the mineral will be levitated in the froth.

With a few exceptions, all clean minerals are completely wetted by pure water. Thus the art of flotation consists in adding substances to the water to make a finite contact angle with the mineral to be floated, but to leave the other minerals with a zero contact angle. The contact angle concept and experimental measurements of contact angles have played important roles in flotation research for several decades.¹⁻⁵ Nevertheless, there remain unanswered some basic questions as to the scientific significance of the contact angle and the nature of the processes by which flotation reagents affect contact angles.

The contact angle is a complex quantity because the properties of three different phases, or rather of three different interfaces, control its magnitude. Considering the interfaces close to the region of ternary contact to be plane, the relation among the contact angle and the three binary interfacial tensions is easily derived. The condition for equilibrium among the three surface tensions, Fig. 1, or the requirement of minimum total surface free energy leads to Young's equation, Eq. 1:

$$\gamma_{SA} - \gamma_{SL} = \gamma_{LA} \cos \theta \quad [1]$$

According to this equation, the contact angle has one well-defined value. Actually it is found in many experiments that the value of the contact angle depends on whether the air is replacing liquid over the solid (receding angle) or the liquid is replacing air (advancing angle). The receding angle is always the smaller of the two.⁴

Two explanations have been offered for this experimental fact. According to some investigators,⁵⁻⁸ roughness of the surface causes apparent contact angles that are different for the receding and the advancing cases although the actual local contact angle may be completely determined by Eq. 1. The other explanation involves the hypothesis that the

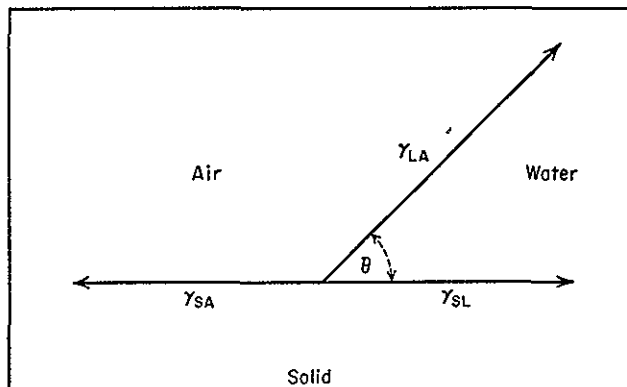


Fig. 1—The three-phase contact.

solid-air interface after the liquid has just receded is different from the same interface when no liquid has previously covered it.^{3,4} Adsorption of constituents of the air or liquid might play a role here.

In this discussion the difference between advancing and receding contact angle will be neglected and plane surfaces where Eq. 1 describes the situation will be considered. But there is still a fundamental obstacle to the application of Young's equation. The surface tension of the liquid (γ_{LA}) can easily be determined, but the two surface tensions of the solid (γ_{SA} and γ_{SL}) cannot be measured directly. Eq. 1, however, is not without value. By contact angle measurements it is possible to establish how $\gamma_{SA} - \gamma_{SL}$ varies with the addition of solutes to the liquid phase. Also, Eq. 1 affords a convenient starting point for calculating net forces and energy changes involved in the process of bubble-particle attachment.^{1,9} If for the moment surface tension of the liquid (γ_{LA}) is considered a constant, an increase in $\gamma_{SA} - \gamma_{SL}$ will tend to decrease the contact angle. A decrease in $\gamma_{SA} - \gamma_{SL}$ corresponds to an increase of the contact angle. In cases where $\gamma_{SA} - \gamma_{SL} > \gamma_{LA}$ the contact angle is zero; it will only reach finite values when $\gamma_{SA} - \gamma_{SL}$ has been decreased below γ_{LA} . Thus on the basis of Young's equation and contact angle measurements alone, it can be learned how flotation reagents affect the difference $\gamma_{SA} - \gamma_{SL}$, but no conclusions can be drawn as to the effects of reagents on the individual surface tensions γ_{SA} and γ_{SL} , not even as to signs or directions of the surface tension changes resulting from reagent additions.

A quantitative relationship between the surface tension or interfacial tension and the adsorption occurring at a surface or an interface is given by the Gibbs equation, which for constant temperature and pressure reads

$$d\gamma = - \sum_i \Gamma_i d\mu_i \quad [2]$$

where $d\gamma$ is the infinitesimal change in surface tension accompanying a change in chemical potential

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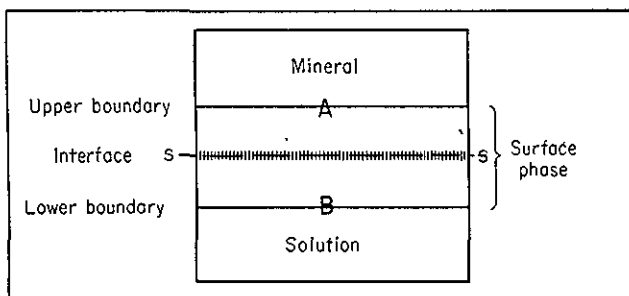


Fig. 2.—The surface phase between mineral and solution. Planes A and B are on each side of the interface, sufficiently distant from the interface that the portions of the system not included between them can be regarded as completely homogeneous bulk phases. The mathematical dividing surface SS is usually chosen in such a way that the surface excess of the solvent is nil.

$d\mu_i$ of the component i of the system and Γ_i is the number of moles of component i adsorbed per cm^2 of surface.

In dilute solutions, the chemical potential of a solute is given by the expression

$$\mu_i = \text{const.} + RT \ln c_i \quad [3]$$

where R is the gas constant, T the absolute temperature and c_i the concentration of component i in the bulk solution. The "const." depends on the solvent and on the units of concentration but not on the other solutes that are present in small amounts.

For the derivation of Eq. 2 the reader is referred to the literature.^{4, 10, 11} If this equation is to be used intelligently, it is necessary to be explicit about the meaning of Γ and also to define correctly the components of the system to which the summation applies. Moreover, it should be emphasized that the Gibbs equation is applicable only when the surface is in equilibrium with the bulk phases.

Gibbs¹⁰ pointed out in his fundamental treatise that the adsorption of any one substance cannot be defined in an absolute way. The adsorption of one chemical species can be expressed only in terms of that of another species. The amount adsorbed (Γ_i) may be defined as the excess amount of substance i present in the surface phase, that is, in the interface (or surface), plus the adjacent regions of the bulk phases, see Fig. 2. This excess is equal to the amount of substance i in the surface phase minus the amount of i which would have been present if the volume occupied by the surface phase were filled instead with the two homogeneous bulk phases separated by a mathematical surface. Defined in this way, Γ_i varies with the choice of position for the mathematical surface, since this choice determines the relative amounts of the two bulk phases which would theoretically have to be used to fill the volume of the surface phase. This uncertainty in the definition of Γ_i does not affect the value for the change in surface tension ($d\gamma$) in Eq. 2, because in the bulk phases the Gibbs-Duhem relation^{12, 13}

$$\sum_i n_i d\mu_i = 0 \quad [4]$$

is valid, where n_i is the number of moles of component i per unit volume. It is therefore immaterial where the mathematical dividing plane is placed or how much of the bulk phases is considered to belong to the surface phase. Often this plane is conveniently chosen so that one component, usually the solvent,

is not adsorbed at all but belongs completely to the solution phase, see Fig. 2. This convention actually corresponds to the analytical definition of adsorption ordinarily used in experimental studies of adsorption from dilute solutions. Therefore, the summation in Eq. 2 must be extended to all components of the system including the mineral itself or to all components except the solvent if the assumption is made that the solvent is not adsorbed.

A further important point to consider is whether ions or neutral substances should be chosen as the components of the system. In principle this choice does not affect the final result, but since different ions as a rule are not adsorbed in equivalent amounts, it is often preferable to consider ions as the components. However, electroneutrality must be preserved both in the bulk of the solution and at the interface, and therefore the number of independent components is one less than the total number of ionic species present. Usually one or more relations exist among the chemical potentials of ions which further restrict the number of variables; for example, $\mu_{H^+} + \mu_{OH^-}$ is a constant and the solubility product of the mineral is a constant.

The relations can be handled very simply as follows: First write the Gibbs equation, Eq. 2, and consider the summation to be carried out for all ionic and neutral components except the solvent. Then introduce the principle of electroneutrality in the Γ 's, use the relations among the chemical potentials to reduce the number of variables, and finally combine the chemical potentials of ions into those of salts, thus taking the electroneutrality of the solution into account.

Application to Flotation: Flotation systems usually contain such a large number of components that writing down the complete Gibbs equation for them, though not impossible or even difficult, would be tedious. Fortunately, in most cases what happens during simultaneous changes of all the chemical potentials is not of interest, but rather the effects produced by the addition of a single substance (collector, activator or depressant) to the system.

The Gibbs-Duhem relation, Eq. 4, shows that the chemical potential of one component cannot be altered without changing at least one of the others. In a dilute solution, however, the addition of a small amount of substance A to the system can be considered to change only the chemical potential of this component and that of the solvent. The chemical potentials of all the other components remain unchanged. Furthermore, the mineral is present as a separate phase and has, therefore, a constant chemical potential. When chemical reactions between the added substance and one or more of the other components occur, more complete forms of the Gibbs equation have to be considered.

The application of the Gibbs equation to a flotation system presupposes that equilibrium is attained or at least closely approached. Thus if the Gibbs equation is found consistent with experimental facts on actual systems, such agreement may constitute indirect evidence of attainment of equilibrium.

Influence of the Collector. A Simple Collection System: First to be considered is the addition of a collector that does not give rise to any chemical reactions or precipitations of insoluble phases. The solution already may contain any number of solutes which may or may not be adsorbed at the surface, but the concentrations and chemical potentials of these solutes will be kept constant.

If the collector is a neutral molecule, X, the Gibbs equation for addition of the collector would be

$$d\gamma = -\Gamma_X d\mu_X - \Gamma_{H_2O} d\mu_{H_2O} \quad [5]$$

On the other hand, if the collector is an electrolyte, say C^+X^- , where X^- is the active collector ion and C^+ an inorganic cation like Na^+ , H^+ or NH_4^+ , the Gibbs equation will contain three terms,

$$d\gamma = -\Gamma_X d\mu_X - \Gamma_{C^+} d\mu_{C^+} - \Gamma_{H_2O} d\mu_{H_2O} \quad [6]$$

In Eqs. 5 and 6, the last term, $\Gamma_{H_2O} d\mu_{H_2O}$, is zero, if the convention is used that the adsorption of the solvent (Γ_{H_2O}) is zero. Usually, the second term in Eq. 6 can be neglected either because the adsorption of the cation (Γ_{C^+}) is small or because the concentration of the cation is already determined by the presence of an inorganic salt so that $d\mu_{C^+}$ is negligibly small.

It might be argued that if the collector ion is adsorbed by an ion exchange mechanism as demonstrated for chalcocite by Gaudin and Schuhmann¹⁴ and for galena by Taylor and Knoll,¹⁵ a term or terms for the exchanged anions (SO_4^{2-} , OH^- , CO_3^{2-}) should be added to Eq. 6. These terms, however, will be small, especially if the volume of the solution is large compared to the amount of mineral. The number of anions released to the solution by this ion exchange will hardly change the concentration of these anions in the solution; therefore, the relevant $d\mu$'s are very small and may be neglected.

In all cases of flotation, the collector is positively adsorbed to the mineral. This means that Γ_X or Γ_{X^-} is a positive quantity if Γ_{H_2O} is considered to be zero.

Consequently, according to Eqs. 5 and 6, the addition of a collector lowers the interfacial tension γ_{SL} between mineral and solution.

According to Eq. 1 and Fig. 1 this decrease of γ_{SL} would lower the contact angle. Experiments, however, show an increase in the contact angle under these conditions. The experimental observation cannot be explained by an increase in the surface tension γ_{LA} , which, if affected, decreases slightly on addition of the collector. Neither can failure to reach equilibrium at the mineral-solution interface account for the increase in contact angle because this would only make the change in interfacial tension smaller and would not reverse its sign.

The conclusion is apparent, therefore, that in the collector system considered here the increase in contact angle has to be explained by a decrease of the surface tension mineral-air (γ_{SA}), a decrease which has to be larger than the decrease in γ_{SL} .

The decrease in the surface tension mineral-air is evidently brought about by adsorption of the collector to that surface. If the mineral-air interface is in equilibrium with the solution, the chemical potential of the collector should be the same at the mineral-air and the mineral-solution interface. A larger change in γ_{SA} than in γ_{SL} then demands a higher adsorption of the collector at the solid-air interface.

This analysis indicates that a collector should show not only a special affinity for the mineral, but in addition a tendency to prefer the mineral-air to the mineral-water interface. It should have, therefore, a strong hydrophobic group. As bases of an opinion on the qualities and possibilities of collectors, adsorption studies at the mineral-solution interface are certainly valuable and important, but for a good understanding of flotation more information on ad-

sorption at the mineral-air interface seems indispensable.

Precipitate Formed by Collector. A More Complex System: Analogous conclusions are reached in the somewhat more complicated system where the collector ion forms a precipitate with one of the ions furnished by the mineral. Especially in xanthate flotation of sulphide minerals does this situation sometimes occur.¹⁴ Taggart and Hassialis¹⁶ have suggested that the solubility product of the compound between the collector ion and an ion from the mineral must be reached if collection is to occur. Without committing themselves to this point of view, the authors wish to show how the Gibbs equation must be treated in the case of precipitation.

Assume a system consisting of a mineral M^+A^- , a collector Na^+X^- , a salt Na^+B^- and water. The compound M^+X^- is assumed to be only slightly soluble and the amount of salt is large enough that addition of NaX does not change the chemical potential of the sodium ion. For the process of adding collector to this system the essential form of the Gibbs equation is

$$d\gamma = -\Gamma_{M^+} d\mu_{M^+} - \Gamma_{A^-} d\mu_{A^-} - \Gamma_X d\mu_X - \Gamma_{H_2O} d\mu_{H_2O} \quad [7]$$

When both M^+A^- and M^+X^- are present as solid phases, the constancy of the solubility products can be expressed:

$$d\mu_{A^-} = -d\mu_{M^+} = d\mu_X \quad [8]$$

With the assumption of zero adsorption of H_2O , Eq. 7 then becomes

$$d\gamma = +(\Gamma_{M^+} - \Gamma_{A^-} - \Gamma_X) d\mu_X \quad [9]$$

and with the condition of neutrality of the surface

$$d\gamma = (\Gamma_{B^-} - \Gamma_{Na^+}) d\mu_X \quad [10]$$

The value and even the sign of $d\gamma$ thus depend critically upon the detailed composition of the surface. If the adsorption of X^- is essentially an exchange with B^- and the adsorption of Na^+ is negligible, Γ_{B^-} will be positive as long as the exchange is not complete and Eq. 10 indicates that the interfacial tension increases with addition of collector. On the other hand, if the adsorbate is essentially Na^+X^- and the adsorption of B^- is small, Eq. 10 indicates that the surface tension decreases on collector addition.

In either case, however, the change in surface tension at the mineral-air interface is very important. If γ_{SL} goes down, γ_{SA} should go down more in order that a contact angle may develop. But, if γ_{SL} increases, γ_{SA} should increase more slowly. Assuming equilibrium to exist, this again means that Γ_{B^-} on the mineral-air interface should be smaller than Γ_{B^-} on the mineral-solution interface. In either case, an increase in contact angle results from collector addition only if the collector adsorption is greater at the mineral-air interface, just as in the simple collection system discussed earlier.

This example illustrates how important the determination of the adsorption may be, not only of the collector, but also of other components of the system.

Relation to Other Approaches: The usual explanation of collection is that the collector becomes adsorbed on the mineral surface with its hydrophobic end turned away from the mineral, thus leaving the surface hydrophobic or water-repellent. The same basic considerations are involved in this explanation

and in the approach based on the Gibbs equation. A collector should be easily adsorbed and should contain a hydrophobic part in its structure. The difference between the two approaches lies in the qualitative nature of the explanation based on the hydrophobicity of the surface as opposed to the quantitative character of the approach by the combined use of the Gibbs and Young equations.

Activation: An activator is a solute which promotes the flotation of a mineral by a collector which otherwise would have no effect on the mineral. A generally accepted explanation of activation is that the activating ion is adsorbed on the mineral and acts as a bonding agent between the mineral and the collector.

Several different forms of the Gibbs equation may be used to represent the effects of activators, and the choice will depend on what aspect of activation is being considered and on whether or not side reactions such as precipitation need to be considered.

First, if collection and activation occur without any precipitation reactions,¹⁷ Eqs. 5 and 6, already discussed for simple collection systems, are still applicable in the presence of an activator. However, for minerals requiring activation, Γ_x or Γ_{x^-} and therefore $d\gamma$ resulting from an increase in collector concentration will be small or zero in the absence of the activator. A more informative approach to systems of this kind is obtained by writing the Gibbs equation for the process of increasing activator concentration, while keeping the concentrations and chemical potentials of the collector and of other solutes constant. To be specific, consider a system comprised of a mineral, a collector Na^+X^- , an activator Z^+Cl^- , and other solutes under conditions of no precipitation, complex-ion formation, or other side reactions.

The Gibbs equation for the process of adding activator then becomes

$$d\gamma = -\Gamma_{z^+} d\mu_{z^+} - \Gamma_{\text{Cl}^-} d\mu_{\text{Cl}^-} - \Gamma_{\text{H}_2\text{O}} d\mu_{\text{H}_2\text{O}} \quad [11]$$

If chloride adsorption is negligible ($\Gamma_{\text{Cl}^-} = 0$) or if initial chloride concentration is large enough that the activator addition causes no appreciable change in chemical potential ($d\mu_{\text{Cl}^-} = 0$), and if the convention $\Gamma_{\text{H}_2\text{O}} = 0$ is used, the Gibbs equation for activator addition simplifies to

$$d\gamma = -\Gamma_{z^+} d\mu_{z^+} \quad [12]$$

Thus, for this simple system in which it is postulated that no precipitation or other side reaction occurs, the addition of activator *lowers* the surface tensions of the solid. If the activator addition is effective in increasing the contact angle, clearly the adsorption of activator (Γ_{z^+}) must be greater at the mineral-air surface than at the mineral-solution surface. Since it would not be expected that activating ions by themselves would show any special tendency to accumulate at the mineral-air surface, it must be concluded that a greater adsorption of activator at the mineral-air interface is the result of the fact that the activator and collector are jointly adsorbed, each strongly affecting the adsorption of the other.

A common characteristic of activator-collector pairs is their tendency to react metathetically to form highly insoluble precipitates, and flotation has been observed under conditions where such reaction products are present.¹⁸ For the system in which the collector Na^+X^- and the activator Z^+Cl^- react to form

a precipitate ZX , the equilibrium of the solution with the precipitate requires that

$$d\mu_{z^+} = -d\mu_{x^-} \quad [13]$$

The Gibbs equation for addition of activator to this system then becomes

$$d\gamma = -\Gamma_{z^+} d\mu_{z^+} - \Gamma_{\text{Cl}^-} d\mu_{\text{Cl}^-} - \Gamma_x d\mu_x - \Gamma_{\text{H}_2\text{O}} d\mu_{\text{H}_2\text{O}} \quad [14]$$

Omitting the terms for Cl^- and H_2O for reasons given earlier, and combining Eqs. 13 and 14

$$d\gamma = -[\Gamma_{z^+} - \Gamma_x] d\mu_{z^+} \quad [15]$$

If the activating ion has valence n and forms with the collector a precipitate ZX_n , Eq. 15 would become

$$d\gamma = -\left[\Gamma_{z^+} - \left(\frac{1}{n}\right)\Gamma_x\right] d\mu_{z^+} \quad [16]$$

Eqs. 15 and 16 show that the direction of change of the surface tension on the addition of activator depends on the number of equivalents of activator and collector adsorbed. If the number of equivalents of activator adsorbed is greater than the number of equivalents of collector adsorbed, then the addition of activator is effective in reducing surface tensions of the mineral. Conversely, if the equivalents of collector adsorbed exceed the adsorbed equivalents of activator, the surface tensions of the mineral will be increased.

According to previously held views of the nature of activation, an effective activator is bonded both to the mineral and to the collector so that the valence of the activating ion must be divided between the collector and the mineral. That is, the number of equivalents of activator adsorbed is expected to exceed the number of equivalents of collector adsorbed. For example, Gaudin and Rizo-Patrón¹⁹ have suggested that quartz flotation with oleic acid and barium chloride involves the adsorption of equimolar quantities of Ba^{++} and $\text{O}1^-$, or two equivalents of Ba^{++} per equivalent of $\text{O}1^-$. For this system, the expression in brackets in Eq. 16 will be positive and the effect of adding barium is to reduce the surface tension at both the mineral-air and mineral-liquid interfaces. To account for the increase in contact angle obtained by adding Ba^{++} , it must then be concluded that the adsorption of Ba^{++} and $\text{O}1^-$ or of the combination $\text{BaO}1^+$ must be greater at the air-mineral interface.

As more experimental data become available, it may become desirable to consider still other forms of the Gibbs equation for activation processes. For example, another possibility not considered above is an activator-collection system in which the activator and the mineral react to form a precipitate phase.

Depression: A depressant prevents flotation in a system where flotation would otherwise occur. The depressant therefore makes the contact angle decrease to zero.

A simple explanation of depressant action is obtained on the assumption that the depressant is adsorbed at the mineral-water interface but does not show any tendency to go to the mineral-air interface. According to this picture the depressant will lower γ_{st} , without affecting γ_{sa} too much. Such a behavior might be expected from hydrophilic, high molecular weight substances like starch which are used in potash and iron ore flotation operations.

Some electrolytes may act as depressants because they furnish ions which compete with the collector

ions and replace the collector at the mineral surface by ion exchange adsorption. In the absence of side reactions, the Gibbs equation for the process of adding depressants of this kind is essentially the same as for adding collector (Eq. 6 with X^- a depressing ion instead of a collecting ion) and leads to the reasonable conclusion that the contact angle is reduced if the depressing ion is more strongly adsorbed at the water-mineral surface than at the air-mineral surface. This results in the extremely interesting hypothesis that both collectors and depressants may lower the surface tensions of both the mineral-water and the mineral-air surfaces, so that the difference between collection and depression, or between flotation and non-flotation, depends primarily on whether the added reagent tends to adsorb more at the mineral-air surface or more at the mineral-water surface. It therefore becomes of great interest that experiments be devised to compare adsorptions at the two mineral interfaces, for depressants as well as for collectors.

Depression by deactivation, e.g., cyanide depression of copper-activated sphalerite, can be considered in terms of Eq. 12, provided the depressing agent is not itself also adsorbed on the mineral. That is, the depressant reacts with the activator (complex-ion formation or precipitation) to reduce the chemical potential of the activator. To refer to Eq. 12, $d\mu_{z+}$ will be negative and the changes in γ_{SL} , γ_{SA} , and the contact angle will be of opposite sign from those for activation when $d\mu_{z+}$ is positive.

Lack of Equilibrium at the Solid-Air Interface: Even if the mineral-solution interface reaches equilibrium readily, equilibrium is not necessarily reached at the mineral-air interface. The available data do not give any indication whether equilibrium is reached or not, except in so far as the difference found between receding and advancing contact angles suggests lack of equilibrium.

Under non-equilibrium conditions the straightforward application of the Gibbs equation is no longer possible. If, however, it is possible to determine the composition of the solution with which the surface would be in equilibrium, the surface tension could be calculated by assuming that the adsorption was built up in a reversible manner. The following integral then gives the surface tension

$$\gamma_{SA} = \gamma_{SA}^{\circ} - \sum_i \int_{\mu_i=0}^{\mu_i^{eq}} \Gamma_i d\mu_i \quad [17]$$

where γ_{SA}° is the surface tension of the surface in the absence of adsorbing solutes ($\mu_i = 0$) and the integral is supposed to follow only equilibrium conditions. The upper limit of integration, instead of containing the chemical potentials in the actual solution, contains the chemical potentials μ_i^{eq} corresponding to the actual adsorption. This integration requires information on the equilibrium adsorption isotherm, that is, data showing how Γ_i varies with μ_i under equilibrium conditions.

If adsorption equilibrium is approached both at the water-mineral and at the air-mineral surfaces under actual flotation conditions, it must be concluded that the adsorbed substances on both interfaces possess a high degree of mobility. The authors' analyses in terms of the Gibbs equation and the Young equation indicate that flotation depends on the existence of differences in adsorption densities between the part of the mineral surface in contact with air and the part in contact with water. Thus, as air spreads over a mineral surface, displacing

water, the quantity of adsorbed collector should increase. The recent work of Hassialis and Myers²⁰ has shown a degree of mobility of adsorbed collector that may account for such an increase.

Conclusion

The principal value of applying the Gibbs adsorption equations to flotation systems is that the results point directly to the need for experimental work in several hitherto neglected areas of the surface chemistry of flotation. Above all, the relations developed by combining the Gibbs equation with the Young equation show that more attention should be given to the mineral-air interface.

To develop further the application of the Gibbs equation to flotation systems, simultaneous measurements should be made of contact angles and adsorption isotherms on both mineral-air and mineral-solution interfaces. Since it is probable that equilibrium at the mineral-air interface will be difficult to achieve and to measure, the use of volatile collectors, e.g., mercaptans, may be advantageous. Another possible experimental approach is to use a liquid mineral to obtain a system in which the three surface tensions could be determined directly. The system water-mercury-gas, with addition of collectors and other flotation agents, suggests itself for these measurements.

Finally, the question of attainment of equilibrium at the mineral-air interface highlights the desirability of further studies of mobility of adsorbed species, contact angle hysteresis, and related topics.

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Safety in the Mechanical Mining of Coal

by W J Schuster

Safety in coal mines depends largely upon adequate training of the foreman. Although management must provide modern and safe equipment and at all times keep mines in first class condition from a safety viewpoint, final results will be determined by the quality of supervision.

HANNA COAL CO., Division of Pittsburgh Consolidation Coal Co., operates three large underground mines in eastern Ohio. The section of Pittsburgh No. 8 coal seam in which these mines are located varies in thickness from 52 to 64 in. It is immediately overlain by a stratum of shaly material 12 to 15 in. thick locally known as draw slate, which is structurally very weak and which disintegrates rapidly upon exposure to atmosphere. Immediately above the draw slate as it is normally found is a band of extremely high ash material 6 to 12 in. thick known as roof coal or *rooster coal*, and above this is a stratum of conglomerate material varying from 4 to 10 ft in depth. Overlying the conglomerate is a relatively thick stratum of limestone, the first stable material above the Pittsburgh coal seam in eastern Ohio. With the method of full-seam mining that has been adopted, draw slate is shot down, loaded with the coal, and removed in the preparation plants. The roof coal then becomes the permanent roof.

The major problem in mining the No. 8 seam in eastern Ohio is control of the roof. Since the strata above the draw slate contains no material with a structure firm enough to provide self-support, the roof begins to sag in a relatively short time after the coal and draw slate have been removed. The problem thus becomes one of getting temporary safety posts under this roof as quickly as possible to prevent a break or separation from occurring either in the roof coal or in the conglomerate above it.

Haulage System

The Pittsburgh No. 8 seam in eastern Ohio is relatively level, with only minor local dips. Throughout the Hanna Coal Co. mines, entries are generally 12 ft wide. Rooms are driven on a 60° angle on 30-ft centers and are 22 ft wide. No attempt is made to extract the 8-ft pillars between.

The entire length of main line haulage is gunited in one mine, and a major portion in another. Two

of the mines have single-track main haulage roads with passways. The third, a new mine, is double-tracked, and the roof is supported by steel crossbars, 60 lb or heavier, spaced on 4-ft centers and lagged. In recent years timbering on main line and secondary haulage roads has been accomplished by one of two methods: 1—crossbars are supported on a small section of post set in a hitch hole in the rib, or 2—or a hole is drilled in the rib about 12 in. below the roof, of sufficient depth to fasten securely a short length of 40-lb rail, the bottom of the rail facing the roof, on which a short post is set directly under the crossbar. At present the hitch-hole timbering method is favored.

At two of the mines the main line haulage locomotives are 2-ton, 8-wheel units. These locomotives are of the axleless type, each wheel being individually mounted on the frame. The motorman's compartment is encircled by 3-in. armor plate for the protection of the occupants.

At the third underground mine conventional 15-ton locomotives are being used. However, these locomotives have been completely rebuilt in the company's shops. Equipment has been streamlined and quarters have been provided for two people, who are protected by heavy steel plate in much the same way described above. This modernization program has been completed on all secondary haulage locomotives at the three mines, and the company is well on the way to similar equipment of the 6-ton section locomotives. The following additional features have been included in their modernization: 1—additional support for the motors to prevent their falling to the middle of the track and derailing the locomotives should a break occur in the suspension bar support; 2—installation of additional bracing to prevent brake rigging from becoming displaced and causing derailments; 3—enclosure of all electric wiring in conduit or raceway; 4—provision of an enclosed compartment for the storage of re-rallers, jacks, and other equipment, so that they need not be carried on the outside of the motor; and 5—redesign of the end of the locomotive opposite the operator's compartment to prevent anyone's mounting from that direction. It is interesting to note that some

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