WETTING AND ADSORPTION IN LITHOGRAPHY

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INTRODUCTION

Lithography is a chemical method of printing (1) but the many advances in chemical science since its discovery have left it almost unaltered. (2) Probably the most important principle of lithographic processes is the ink, water theory which states that ink and water will not mix or are repellant and that therefore their distribution on a solid surface will not change spontaneously. (3) An ink is a greasy or oily substance consisting chiefly of linseed varnish and a pigment. (4) Ink and water do not repel each other but when in contact are held together by an attractive force which in many cases is greater than the cohesive force within the ink itself. (5) Ink and water are not misicible but they are sufficiently soluble in each other to enable changes to occur with fair rapidity if that change is accompanied by a decrease in free energy. The water and the ink used in lithography must be immisicible but many additional properties are necessary. In order therefore to explain a lithographic process it is necessary to consider the methods and materials which are used with regard to their effect on the properties of the printing plate.

GRAINING

The processes of lithography are graining, counteretching, preparation of image, etching, and printing. In the graining operation the only change which occurs is an in-

crease in the area of the plate. (6) To a lithographer the chief function of a grain is to enable a plate to hold more water or more ink. It serves this purpose but the main function is to maintain a continuous film of water on the non-printing portions of the plate. A grained plate after standing in the air for months is wet at all points by water but a polished plate after standing in the air for a few minutes will not be wet by water over a large part of its area. In both cases the area of the water will equal the area of the plate not considering the irregularities in the surface since the water will completely fill these irregularities. When wetting just fails to occur the increased surface energy caused by the removal of the water must equal the surface energy which disappears. If the actual area is a sufficiently high multiple of the over all area even a small increase in free surface energy produced by the removal of the water, when multiplied by the true area, will be greater than the surface energy of the water film. It is obvious that with a sufficiently fine grain a paraffine surface would retain a continuous film of water. From the above theory two important conclusions can be drawm. Any surface with a sufficiently fine grain will be wet at all points by a liquid. The presence of thin films of oil on a grained surface will not prevent wetting. The latter conclusion has been confirmed exprtmentally. A grained surface on which oil of lavander and nitrobenzene could

still be detected was wet at all points by water. The experiments of Devaux (7) show that a polished surface is not wet by water in the presence of less than a monomolecular film of oil.

COUNTERETCHING

When a plate is counteretched it is usually washed with a dilute solution of a strong acid. The function of this process " is to cause the plate to have a greater affinity, or susceptibility, to the greasy ink". (8) This statement while common to most books on lithography is probably incorrect. Counteretching should be considered as only a cleansing process. (9)

THE IMAGE

An image is that portion of the printing plate which is covered with ink. Usually the image will consist of dots about .004 inches in diameter. All of the various methods in use for obtaining an image seem to give plates of about the same life. This may indicate that the life of the plate does not depend on the relative affinities of the ink or of the basis of the image for the plate.

ETCHING

Etching is a method of giving to the non-printing portions of the plate water receptive properties. The printing plate after the etching operation can be regarded as a metal surface partly covered with a substance preferentially wet by water and partly by a substance preferentially wet by

ink. These substances which are probably adsorbed on the plate tend to prevent any change in the water or ink areas. (10) This method of explaning the facts is more nearly in accord with modern theory than the chemical reactions proposed by most writers on lithography. Preferential wetting must be considered since the presence of a monomolecular film of grease or oil on the plate would not prevent wetting by water but may result in a gradual increase in size of the image.

An etch probably acts in the following manner. It is adsorbed and forms on the metal plate a film which is preferentiallywet by water. If the plate drys at any point or if lose particles of ink are deposited on the plate the etch forms a film between the ink and the plate. On the subsequent addition of water the upper layers dissolve in the water and carry off the ink. When the film becomes thin and difficultly soluble the ink is removed with difficulty. The valuable properties of an etch depend therefore on its ability to take up water after drying on a plate.

Etches are unnecessary whenever the non-printing portions of the plate are covered with a film of a hydrophilic substance. In the acquatone process (11) and the new process recomended by the Lithographic Technical Foundation (12) there is obtained on the non-printing portions of the plate a thick film which can absorb considerable water. Ink placed on the dry film can easily be removed by washing. Both the above processes and the etching process result in

the production of a hydrophilic film on the plate but in the etching process the film is extremely thin and easily destroyed. These processes are therefore superior to any method of etching.

PRINTING

Printing is the test of the efficiency of the methods of preparing the image and of etching for producing a stable condition on the printing plate. The image can change in a number of different ways. It can increase or decrease in size gradually. It can "walk-off or disappear through a failure of the plate to regain the ink it loses during the printing operation. The plate can tint through the deposition of ink on the water wet areas. It is possible that each change could be produced in a number of ways but in most cases only one cause will be present. The following mechanical pictures will serve as a possible explanation of some of the phenomena observed during printing.

At the point of contact of the ink and water the surface tension of the water tends to pull it away from the ink image. If the material forming the water attractive surface is not present in sufficient quantity the amount of water at the border of the ink image may be insufficient to prevent its growth through the mechanical flattening of the image produced by the ink rollers. If the metal surface preferentially adsorbes the oil of the ink the water will draw away from the image border and there will be a gradual in-

crease in the size of the image. In both cases the mechanical influence of the ink roller must produce the increase in size since flowing can not occur. (13) High pressure, easily flowing inks, or a large amount of ink may be factors in producing an increase in the size of the inked image as well as a preferential affinity for ink. In the presence of acid the image size may be decreased through solution of the metal. Films of ink and similar substances permit the free passage of ions of small size and therefore the acids used on the plate will be able to attack the metal under the center of the dot as well as at the border but it is only at the border that there is sufficient water present to create new water wet areas. If the water preferentially wets the metal surface, then at the border between the ink and water the water will gradually form a thin film under the ink. This film will not be sufficiently thick to possess the fluidity of the film on the non-printing portions of the plate and because of its large area compared with the overall dimensions of the plate it will hold the ink with a greater force than its breaking strength over this area. Even with a thin film of water between the ink and the plate printing would be possible but if the supply of ink was limited there might be a slight decrease in size at the border.

As the ink roller passes over the image the ink forms a continuous phase from plate to roller. If this phase is uniform the plate will in each revolution take up the ink

it has lost and a decrease in the intensity of the image will be caused by a decrease in the amount of the ink supplied by the ink roller. When the ink supply remains uniform the gradual decrease in intensity must be caused by an accumulation of foreign material on the ink which prevents the formation of a uniform phase on contact with the ink roller. The removal of a large portion of the ink from the plate during the printing operation will give a surface on which water will more easily form a continuous film. The presence of a large amount of water or the presence of gas bubbles in the ink produced by the action of the acid in the fountain water will aid in causing this fading of the image.

When a cylinder of paraffine revolves in water its surface carries the water with it in the direction of its rotation. Some of the water remains on the paraffine in the form of drops while the rest flows back into the main body of the liquid. A somewhat similar case would be two cylinders of different liquids revolving in contact. The internal pressure of all liquids is very high so that with liquids flowing rather than breaking occurs wherever possible. A pure homogeneous liquid will flow under the smallest impressed force. At the point where the liquids separate flowing will occur in the liquid which imposes the least resistance. The resistance to flowing will be proportional to the rate of deformation or flowing and to the viscosity and plastic strength of the liquid. In the case of water and

ink or mercury and ink the water and the mercury possessing a zero plastic strength and a low viscosity are carried along by the ink with the result that the plate loses mercury or water, but does not acquire ink on the water or mercury areas. It is therefore necessary that the liquid on the non-printing portion of the plate possess a lower viscosity and a lower plastic strength than the ink used. The liquid on the non-printing portions of the plate must not wet the ink, since if it does, it will form a continuous film on the ink and prevent its transfer to the plate. It is obvious, from the above considerations, that the magnitude of the interfacial tension water-oil is of little importance. When the water film becomes thin or the ink becomes less viscous or less plastic, there will be an increased tendency of the non-printing parts of the plate to acquire a coating of ink. Points of corrosion, since they destroy the grain and give high points on the plate, will aid in producing new ink areas on the plate.

Wetting, if the above assumptions are made, is chiefly of importance in the gradual increase in the size of the image the other changes being produced chiefly by the ink. The factors influencing wetting will be considered in detail in the experimental and theoretical portions of this thesis.

The permanence of the image on the printing plate will depend on the kind of surface, type of ink, and the material used on the non-printing portions of the plate. A great

many different types of surfaces have been suggested and used. Wood, leather, rubber, paper, stone, and metal under suitable conditions, form satisfactory printing surfaces (14). In the clean dry state each is capable of acquiring a film of ink which can be removed only with difficulty. The remainder of the plate is etched to impart to it hydrophilic properties.

The life of a printing plate is dependent on the life of the grain and of the film on the plate. In the absence of excessive friction the life of the grain should be very long. The film on the non-printing part of the plate will slowly be removed by abrasion and solution in the water used. It could be replaced a number of times before the grain disappears. The force of adhesion to the plate of the ink, water, and any films which may be present, is probably of only secondary importance, since it is sufficiently high to prevent their removal during printing.

In the theoretical and experimental portions of this thesis, the methods of production and properties of various kinds of films will be considered in greater detail.

HISTORICAL

Lithography was discovered in 1799 by Alois Senefelder(15). It developed rapidly in Germany, and soon spread to France, Austria, England, and the United States (16). From an artistic standpoint, the lithographs of these early days were the equal of those produced today (17). The printing surfaces and the printing materials of today are not much better than those of the infant industry and very little more is known about them. The growth of the industry was made possible through the discovery of better mechanical methods, and not through the application of scientific principles to the methods in use.

Practically every possible kind of solid surface has been used as a planographic printing surface. The first substance to come into general use was a close-grained limestone found at Solnhofen, Bavaria (18). Its valuable qualities were discovered by Senefelder, who used it in most of his work. Many other substances were examined by him, but none of them gave as good results as this particular type of limestone. Among the other substances with which he had some success were paper, zinc, and various alloys. The paper was too easily destroyed, and the metals required more care in their use than the stone. Artificial stones have been made by forcing carbon dioxide into calcium oxide in a mold (19). In 1855 Goodyear patented the use of rubber in place of lithographic stones. Properly prepared, wood can also be used (20).

Aluminium has been in use since 1892. Brass, copper, tin, lead, iron, gold, silver, alloys of tin, lead and bismuth, and many other alloys and metals will give satisfactory printing surfaces, although they have not been used commercially. Glass can be used as a printing plate by forming on it an insoluble precipitate which will retain ink (20). A method of printing with leather was developed by Day in 1908. The materials at present in use are chiefly zinc and aluminium plates, although a few plants still use stones.

The use of a printing plate consisting of two different metals, in which the surface of one metal forms the printing surface and the other metal the non-printing surface, is a comparatively recent development. None of the combinations suggested have been used to a great extent although theoretically a bi-metallic plate should be an improvement over a plate composed of only one metal. In 1873 Friedlander (21) proposed depositing a thin layer of tin, lead, or copper on a metal plate by electrolysis. The non-printing portions of the plate were then removed with an etch. Villon in 1891 used nickel-plated zinc. Rolfs (1901) plated a piece of steel with nickel or copper and then removed the nickel or copper from the non-printing areas. A great many other bi-metallic combinations have been suggested.

The mercurographic or "Pantone" process is really a bi-metallic process, but since water is not used in the process, it has additional advantages(22). It is sometimes

called dry lithography. In one type of process, the plate is coated with silver, followed by chromium. The image is placed on the plate, the chromium is removed with dilute hydrochloric acid from the parts of the plate not covered by the image, and then the silver is amalgamated with mercury. By printing with an emulsion of mercury in ink, the plate is kept supplied with mercury, this forming the non-printing area.

Recently surfaces produced through light action have been used as printing surfaces. Because of the general use of rotary printing presses, it is necessary to use flexible printing plates. By coating a metal surface with another substance it is possible to retain the desirable properties of the metal and at the same time obtain a better printing surface. Niepce, in 1816 (23), invented the first of the photo-mechanical printing processes, although the first successful process is that of Osborn(24) developed in 1859. In these processes, the non-printing portion of the plate consisted of a metallic or stone surface, while the basis of the image was albumin. This albumin remains on the plate throughout the printing operation (25). Collotype is the first process in which both the printing and non-printing portions of the metal plate are covered with another substance (26). The process depends on the difference in properties of hardened and unhardened gelatine. Recently the principle involved in the use of bi-metallic plates has been applied to the prep-

aration of surfaces through light action(12). The basis of the image is hardened albumin, while the non-printing portions of the plate consist of hardened gum arabic. A combination such as this, represents the ideal type of printing plate, an ink-receptive surface surrounded by a permanent water-receptive surface which has no tendency to retain ink.

The most important chemicals used in lithography are counter-etches, etches, and inks. The counter-etches used today were known to Senefelder. The same applies almost equally to etches and inks. Gum arabic and chromic acid,the two ingredients common to most etches are mentioned in his writings (15). An ink can consist of a great many different substances. Senefelder made thousands of experiments, using every type of substance he could obtain, in order to get satisfactory lithographic inks. He published many of his formulae and these were probably used by many lithographic establishments, since most printers at that time made their own inks. With the development of ink manufacturing concerns, the formulae became secret. The new types of ink ~~which~~ were better, but just how the change in composition affected the life of the plate is not known. It is only recently that the properties and functions of these lithographic materials has been studied in a scientific manner.

The methods and materials of lithography have changed but little since the days of Senefelder. His genius, and the vast amount of experimental work he performed during his life-

time resulted in the development of methods and materials which his contemporaries could hardly hope to improve. Since that time however, the vast increase in knowledge, should have resulted in many new developments and a better understanding of the process. Lack of progress must be due to the failure of the leaders of the industry to realize that constant improvement depends on intensive research guided by scientific principles.

OBJECT OF THIS INVESTIGATION

Lithography has become an important branch of printing because if part of the area of certain flat surfaces is covered with water and the remainder is covered with ink, the distribution of these substance is not changed during the printing operation. The object of this thesis is to develop a scientific theory which will account for the observed lithographic phenomena, and to verify this theory experimentally as far as possible. Because of the great complexity of the problem, it is probable that no one explanation will serve for all the observed phenomena, and for that reason, various theories concerning the behavior of solids in contact with liquids and gases will be considered, and their application to lithography pointed out. An explanation of a lithographic process is of no value in itself, but it will aid in the progress of the industry if it indicates possible lines of development. Wherever possible, therefore, theoretical considerations will be applied to concrete examples.

THEORY

INTRODUCTION

In the scientific study of natural phenomena it is often necessary to use several different theories and various experimental methods. The laws of statistical mechanics are of service in the study of the average motions of molecules or atoms. Where a change in the average kinetic energy of the molecules occurs, the laws of thermodynamics may be applied. Frequently certain properties, such as electrical or surface properties, determine completely the behavior of a system. Since a large part of the time was devoted to finding a way of applying scientific theory to a lithographic problem, that of coexistant oil and water phases on a metal surface, these various points of view will be considered in detail.

Kinetic Theory

MOLECULAR FORCES

Matter consists of molecules which are maintained in equilibrium through the operation of four forces. The thermal pressure plus the repulsive pressure equals the attractive pressure plus the external pressure (27). At all distances of greater than molecular magnitude only forces of attraction have been observed. These forces have been divided into three classes (28); electrostatic, polarization(magnetic), and cohesive(Van der Waals) forces. The electrostatic force arises

through the action of the ions in one substance, e.g., sodium chloride, on the molecules of another substance, e.g., argon. The part this force plays in the lithographic phenomena will be considered in detail later. Magnetic forces arise through the presence of magnetic moments in molecules. These forces are very small compared with the other forces which are present with them, but in the presence of molecules of high electrical moment which can transmit these forces almost undiminished, they become the predominating force at large distances. In most cases, both the electrostatic force and the force of polarization, become almost zero at greater than molecular distances from a solid surface. To account for many observed phenomena such as, surface tension, heat of evaporation, vapor pressure, etc., it is necessary to assume the existence of a cohesive force decreasing relatively slowly with the distance. This force may, and probably does, originate in the electrical properties of matter, but no simple relation has yet been derived connecting the two. A repulsive force which is almost zero, even at molecular distances, prevents the collapse of the system. This repulsive force will be omitted in all later discussion.

VAN DER WAAL'S FORCE

The exact nature of the Van der Waal cohesive force is unknown. Although chemical affinity and chemical energy may depend to a greater or less degree on this force, it is essentially a physical force. For example, in a mixture of

oxygen and ethylene, the pressure was reduced 8.5% below theoretical by the oxygen and the replacement of the oxygen by argon did not change the pressure appreciably (29). This cohesive force in condensed or liquid systems is known as the internal pressure. Recently Lorenz (30) has shown that in alloys or salt mixtures, in the liquid state, the Van der Waals constant A, which determines the cohesive force, is equal to the square root of the product of the constants of the individual members of the mixture. A somewhat similar relation exists between the constants of the members of a gaseous system (31).

The importance of the Van der Waals cohesive force has led to many attempts to calculate it from the fundamental properties of matter. The most successful attempt is that of Deby (32), who has obtained a formula involving the molecular diameter and several electrical properties of the molecules concerned, but because of its complexity it is chiefly of theoretical interest. The method of Lennard-Jones which is based on several assumptions concerning the rate of decrease of the forces involved, is of more practical value. It has been applied successfully to the case of adsorption of the rare gases on several crystal surfaces.

Although the mass and volume of a molecule may not determine its force field, still these quantities are manifestations of this field and they should give a good indication of its magnitude. This is shown by the work of Richards(33)

on the compressibility of the elements. Atomic volume and compressibility of the elements when plotted as functions of the atomic weight, give curves which show clearly the influence of concentration of mass on the force of cohesion. While the electrostatic forces of cohesion or the forces of chemical affinity are produced by the cementing effect of the valence electrons in the atom, the physical force of cohesion originates in the nucleus of the atom and depends only on its mass. The periodic change in physical properties due to cohesion, is caused by the periodic change in atomic volume and electrostatic force, and not by a change in the physical force of attraction. The physical force of attraction as defined above, depends only on the atomic mass, but since the repulsive force will depend on the atomic volume, the resultant attractive force will also depend on the atomic volume. The importance of cohesion in the determination of adsorption is shown by the work of Adams (34). He finds that the variation in the floatability of an ore using an oil foam, follows the Van der Waals cohesion factor.

INTERNAL PRESSURE AND ADSORPTION

At the border of a system, the internal cohesive force produces a surface tension and an adsorption force. The maximum possible adsorptive force should be the same function of the cohesive force for all substances, but due to orientation of the molecules at the surface, and because of the formation of surface

films of different composition from the interior, the actual adsorption force present will be less than the maximum possible value.

When adsorption occurs between two substances which will not react chemically, the force of adsorption will depend only on the internal pressure of the two substances. If various liquids are arranged in the order of their increasing internal pressures, they will be arranged in the order of increasing force of adsorption on a given liquid or solid. The force of adsorption is in this case, the observed force of adsorption plus the internal pressure of the liquid, since all that can be observed is the difference between the force of attraction of one substance for itself and for another substance.

RANGE OF MOLECULAR FORCE

Experimental determinations of the range of molecular force give values ranging from 10^{-5} cm. to 10^{-8}cm. These wide discrepancies can be explained if two attractive forces exist. Wherever the experimental conditions are such that electrostatic forces or forces of secondary valence can be measured, the range is in all cases between 10^{-7} and 10^{-8} cm. Langmuir, from his work on adsorption, concluded that the range of molecular force is 2-5 $\times$ 10^{-8} cm (35). From calculations involving some physical constants, Garver obtains (36) about the same results. From the data of many investigators on the adsorption of gases on charcoal, Williams obtains a value of 4×10^{-8} cm.(37)

In the above experiments low pressures were used, and the almost complete disappearance of force at molecular distances is taken as proof of its complete disappearance at slightly greater distances. This conclusion is incorrect if there exists another force, decreasing relatively slowly with the distance, or if the rate of decrease of the force field suffers an abrupt change at this point. Many experimental investigations indicate that the range of molecular force is relatively high. Hardy(38) has shown that a metal can exert an influence through a thick film of lubricant. The rate of evaporation of water on glass decreases at 5×10^{-5} cm.(39). Films of adsorbed water and methyl alcohol on glass, when measured by optical methods are found to be 3×10^{-7} cm. thick(40). Film thicknesses obtained by wringing flat surfaces together, indicate a force range of 2×10^{-6} cm. (41). The thickness of a film of water on sand (42) and of sulphur dioxide and of ammonia on glass (43) near saturation is 2×10^{-6} cm. A titration method similar to an oil absorption number gives a film thickness of 10^{-5} cm. (44). Other methods (45, 46, 47) give similar results. The only attempt to measure directly the range of attractive force is the experiment performed by Richards (48). He found that an aluminium plate, six centimeters square, at a distance of 10^{-4} cm. from different solids which were capable of reacting with it, attracted it with a force of less than 10-1 dynes. Some experimental work to be discussed later, indicates the existance of films 10^{-6} cm. in

thickness. This is in approximate agreement with the above results.

THE FORCE LAW

The magnitude of the force which acts at any point near a surface, will obviously depend on the force law. Many different inverse power laws have been suggested (49), but each law seems to explain only one or two physical properties. Among the power laws which have been suggested, are an inverse second (50, 51), third (52), fourth (53, 54, 55, 56, 57, 58, 59), fifth (28, 60, 61), sixth (28), seventh (49), and eighth (49, 62) power law. From a theoretical study of the problem, the exponent of the distance in any power law must be greater than five, but the necessary consideration of matter as continuous, in any of these derivations introduces an unknown error. Some further refinements have even increased the necessary value of the exponent to eight (49).

In the experimental part of this thesis, is described a method of measuring the force acting at a point near a surface and of simultaneously estimating this distance. By plotting the log of the force against the log of the distance, a straight line is obtained, whose slope equals the exponent of the force law. The results obtained, indicate an exponent of one. The exponent will necessarily be much greater in the absence of a film. Some calculations made by Nutting from data on the heat of adsorption of water on glass, indicate

that the decrease in force is proportional to the distance(63)

LANGMUIR THEORY OF ADSORPTION

Because of the existance of a universal law of attraction, the concentration of a substance at the boundary of any phase, will be increase by the presence of another substance. Increased concentration at the boundary of any phase is known as adsorption. There will be two limiting cases of adsorption, one in which the concentration of the adsorbed substance is nearly equal to the concentration in the liquid or solid state, and one in which the molecules of the adsorbed substance are too far apart to affect each other appreciably (64).

The surface of a solid, since it consists of molecules, must possess a discontinuous force field, with maximum points near each molecule (65). Since the force field is discontinuous, the concentration of the adsorbed material will be discontinuous. The molecules of the adsorbed substance will be too far apart to affect each other appreciably. This is the adsorption theory of Langmuir (35), which has dominated the field since the time of its promulgation. This theory is, of course, an exact statement of the process of adsorption, only if the range of attractive force is about equal to or less than atomic distances, since otherwise, the field strength would not vary appreciably from point to point on the surface. The experimental work of Langmuir substanti-

ates this very well. The forces acting are called secondary valence forces, and are probably electrostatic forces(28). Under the conditions employed, the removal of the adsorbed substance is equivalent to the dissociation of a chemical compound(66), the dissociation product being a gas. The amount of adsorption is, in such cases as this, equivalent to less than a mono-molecular layer. This in the limiting case mentioned above, in which the adsorbed molecules are too far apart to affect each other. The determining factor in this type of adsorption is the relative rate of evaporation and condensation. In this type of adsorption, no lateral motion is possible (67, 68)

APPLICATION OF THE LANGMUIR THEORY OF ADSORPTION TO LITHOGRAPHY

On a lithographic printing plate, oil and water are in contact with a metal surface. If the relative rates of condensation and evaporation of the oil and water adsorbed on the metal surface are low, then the adsorption theory of Langmuir will be of great importance in a study of lithographic processes. If the relative rates of evaporation and condensation of the oil and water on a metal surface are high, then the equilibrium postulated by the Langmuir theory will be reached almost immediately, and the subsequent reactions will depend on some other factor.

An image on a metal surface is in a stable state,

since, if an aluminium plate , marked with ink, is allowed to stand in air or water for days no appreciable change in the area of the ink can be observed. The plates which were allowed to stand in the air, could not exhibit any change because of the low vapor pressure of the ink (69). The image on the plates immersed in water could have changed as is shown by the following experiments. Water was placed on a film of oil which contained solid particles of a water soluble salt dispersed in it. In a short time the small angular particles became rounded, and after a longer time the larger particles appeared as small crystals in a drop of water. This illustrates the replacement of oil by water. Since the appearance of the corrosion film formed on a zinc plate immersed in a molar solution of chromic acid is changed by the addition of linseed oil to the solution, it is probable that the linseed oil is appreciably soluble in the water. These experiments indicate that the kinetic theory of adsorption as developed by Langmuir, is not of importance in lithographic phenomena, since the equilibrium conditions are reached in a very short time.

ELECTRICAL THEORIES OF MOLECULAR FORCE

Since matter is essentially electrical in nature, many attempts have been made to calculate surface forces and adsorption from known electrical properties of matter. The very successful attempts of Lennard Jones (28) and Debye (32)

have been mentioned. Sutherland (70) has studied the relation between the electrical properties of matter and the force of molecular attraction. Pavlov (71, 72) has attempted to show the influence of electrical forces on adsorption. Tarassoff has obtained an equation connecting the heat of wetting and the dielectric constant (73). Ilün has derived an equation connecting the surface tension of solids with the electrical properties of the adsorbed substance (74).

It is well known that charges tend to acquire a coating of the molecules of the surrounding medium. Ions in water become hydrated (75), while ions in a gas carry with them one or more molecules of the gas (76). The condensation of water on gaseous ions in the Wilson experiment on the path of α rays is an example of this phenomena.

APPLICATION OF AN ELECTRICAL THEORY OF ADSORPTION TO LITHOGRAPHY

In a surface consisting of particles carrying charges, as for example, sodium chloride, there will be a force field which will attract other molecules with a force depending on the distance of the molecule and its dielectric constant. The electrical moment is $M = \frac{(D-1)F}{4\pi}\left(\frac{1}{N}\right)$, where

D = dielectric constant
F = force field
$\frac{1}{N}$ = volume occupied by one molecule

If the field if produced by a unit charge then $F = \frac{e}{R^2}$ or

$M = \frac{(D-1)e}{R^2(4\pi)}\left(\frac{1}{N}\right)$. The force acting on a dipole M is $\frac{2Me}{R^3}$ or $F = \frac{(D-1)e^2}{2\pi R^5}\frac{1}{N}$. The potential energy E equals $\int \frac{(D-1)e^2}{2\pi R^5}\left(\frac{1}{N}\right) dR = -\frac{(D-1)e^2}{8\pi R^4}\frac{1}{N}$.

According to the Boltzmann distribution law the potential energy determines the concentration gradient (77). $N_A = N_{Ao}\, e^{\frac{(D-1)e^2}{8\pi R^4}\frac{1}{N}}$ where N_A equals the concentration at a distance R and N_{Ao} equals the concentration at an infinite distance. In a mixture of two substances, the relative concentration of each near a charged body, can be determined directly, if the volume occupied per particle and the number of particles present are equal in each case. Where a particle of one replaces x particles of the other, the total energy change of x particles will equal the potential energy of one particle times x. For oil and water the following equation is obtained.

$$\frac{N_{water}}{N_{oil}} = \frac{N_{wo}}{N_{oo}}\, e^{\frac{(D_W-1)e^2}{8N_W\pi KTR^4}} \times e^{-\frac{(D_o-1)e^2 N_o N_o}{8N_o\pi KTR^4 N_W}}$$

D_W = dielectric constant of water = 81

D_o = dielectric constant of oil = 3.35

N_W = number of molecules of water per cubic centimeter

N_o = number of molecules of oil per cubic centimeter

$$\frac{N_{water}}{N_{oil}}\quad\frac{N_{wo}}{N_{oo}} = e^{\frac{5.5 \times 10^{-28}}{R^4}}$$

If at a large distance the oil and water are present in equal

proportions, then the ratio of water to oil at a distance R from a charge is for R equal to

5×10^{-8} cm $\quad \frac{N_{water}}{N_{oil}} = 10^{35}$

10^{-7} cm $\quad \frac{N_{water}}{N_{oil}} = 14$

From the above calculations it can be seen that on an ionic surface, water will replace almost entirely the linseed oil simultaneously present. There results are only approximate, since the length of the linseed oil molecule is of the same order of magnitude as the distance over which the adsorption is calculated. The electrical moment is taken as the same over the entire length of the molecule, but due to the presence of active groups, it will vary from point to point on the molecule.

A THEORY OF ETCHES

An etch is a substance which is added to the water fountain for the purpose of preventing the adherence of ink to the non-printing portions of the plate. Some previous experimental work in this laboratory (78, 79) has shown, that many of the etches in common use are adsorbed by the metal. An inorganic etch is, therefore, any somewhat soluble salt which is adsorbed by the metal surface, As shown by the above calculations , ink will not adhere to the surface as long as water is present. When the water evaporates, the etch will be deposited on the plate, giving a protective coat-

ing between plate and ink. On the addition of water, this will dissolve and carry the ink with it, leaving a clean non-printing surface. In the presence of a small amount of etch, the solvent action of water will be slight, and the plate will take ink permanently on drying. Several laboratory experiments proved that the ink on a plate protected by a deposit of an etch, could easily be removed by water. Organic etches will be considered in more detail under protective coatings produced by light action.

The ability of salt-like substances to increase the affinity between liquids in which they are soluble and solids on which they are adsorbed, has been noted by numerous investigators. The affinity of oil for silica in the presence of water is reduced by the addition of acids or bases to the water (80). The number of ions adsorbed by a glass surface is often greater than the number required to form a monomolecular film (81). Lubrication experiments have shown that metals adsorb organic acids from oils and that these are oriented, so that the hydrocarbon group is extended toward the oil (82). The acids in the ink probably act like the etches in the water.

CONTINUOUS FORCE FIELDS

The work of Langmuir shows the existence of an intense discontinuous force field at solid surfaces, but it does not show the absence of a continuous force field somewhat less

in magnitude and decreasing relatively slowly with the distance. There is abundant evidence that in addition to the forces of secondary valence there exists a more uniform force field of long range, which can be compared to the earth's gravitational field. In this field diffusion along the surface occurs. The work of Volmer shows that the resistance of glass to the diffusion of benzophenone on its surface is slightly less than the resistance to diffusion in water (83). This work has been confirmed by Moll (84). The theory of the condensation of metals as derived by Frenkel (85), and experimently confirmed by Volmer (86), and also by Crockroft(77), involves the migration of metallic atoms on a solid surface. The pressure, in these cases, is low, and therefore the film is a gas. When two gases are adsorbed at low pressures, they are adsorbed as gases, since both are adsorbed in amounts depending on their partial pressure, and when the total pressure is increased one is liberated (88). This indicates that at high pressures one gas liquifies liberating the other.

ADSORPTION IN LITHOGRAPHY

The above theories can easily be applied to lithography. The metal forming the plate takes up ions from the water and fatty acids from the ink. Both of these are held by electrostatic forces and are therefore held very strongly. The water preferentially wets the water area and the ink preferentially wets the ink area. At the surface of the water

or of the ink, the concentration of ions and acids is almost zero, since negative adsorption occurs. At the water-ink interface, positive adsorption of fatty acids will occur. At the metal surface, the fatty acids will probably be preferentially adsorbed, since they are capable of reacting with both the metal and its hydroxide. This may cause an increase in the size of the image. If the concentration of acid in the linseed oil is low, the pigment will remove most of it. The presence of acids in the fountain further reduces the concentration of fatty acid ions at the water-ink boundary. If we consider the boundary as pure water and oil then, since the adsorption will be governed by the Van der Waals cohesive force, the water having a higher internal pressure will be preferentially adsorbed by the metal.

The Free Energy of Adsorption

GIBBS THEORY OF ADSORPTION

The most important of the theoretical adsorption equations is that due to Gibbs (89) who stated that at constant composition the free energy change at the border of a phase must equal that in the interior of the phase. The failure of this equation to apply to many cases of adsorption is not due to any deficiency in the theory itself, but to errors in its application. The influence of saturation pressure on adsorption, even where the Gibbs equation is not

used, is generally accepted. The absorption or adsorption of water from the atmosphere by gels or fibrous materials such as gelatin or cellulose, depends on the relative humidity and not on the absolute pressure of the water vapor. Williams (90) showed that various adsorption curves became almost identical when the relative, rather than the absolute pressure, was used in plotting them. The selective adsorption of carbon dioxide from hydrogen by mercury, is not regarded as unusual, since carbon dioxide ia an easily condensable gas.

The free energy change accompanying adsorption can be written in the form $-\Delta F = NRT \ln \frac{a_A}{a_E}$, where a_A is the activity in the adsorbed phase in the absence of adsorbent, and a_E is the activity in the external phase. It is usually allowable to substitute for the activity, the pressure or concentration of the substance being adsorbed. The free energy change causing the adsorption, is a change in surface energy of the adsorbent. This equals y, the change in surface tension. Therefore $Y = NRT \ln \frac{a_A}{a_E}$ or $dy = NRT \frac{da}{a}$. This is the Gibbs adsorption equation.

The adsorption equation used throughout the experimental work is the integrated form of the Gibbs equation, given above. This equation has been derived in a great many different ways. Ercken (91, 92) considering the adsorbed material as present in a gaseous diffuse layer on the ad-

sorbent, applies the Boltzmann distribution law, and obtains an expotential function similar to the Gibbs equation. Polyani (93, 94, 95) obtains from thermodynamic considerations, the same equation. The Gibbs equation has been modified by Porter (96) and Polyani (97). The various different modifications of the Gibbs equation which have been mentioned are given in detail in a very complete summary of the complete subject by Swanard Urquhardt (98). Bancroft, on reviewing the subject, concludes that the Gibbs equation can be applied to adsorption on solid surfaces (99). The data to be discussed later depends on the validity of the Gibbs adsorption equation, and on the existence of poly-molecular adsorbed films.

APPLICATION OF THE GIBBS EQUATION

When a substance is adsorbed from the gaseous state on a liquid or solid surface, the amount of adsorbed material should remain approximately constant over a wide pressure range. A nearly saturated mono-molecular film will be formed in many cases at a low pressure and only near the condensation point will a poly-molecular film be formed. If therefore, the excess concentration of the adsorbed phase at the interface, as calculated from the Gibbs equation, remains constant over a wide pressure range, the equation can be said to apply to this case of adsorption.

The surface tension of mercury has been determined in many ways. The values obtained under different conditions vary with the method used, but if the same method is used throughout the experiment, the results are consistent(100, 101). The best data on the influence of vapors on the surface tension of mercury is that of Iredale (102, 103). In the following table are given his experimental results and the film thickness of the adsorbed vapor calculated from his data using the Gibbs adsorption equation. Similar values are obtained with the other substances used by him. The results show that the Gibbs adsorption law can be applied, and that the free energy change involved in the formation of a mono-molecular film is much greater than the change produced by the addition of all succeeding layers of molecules. In the following table N is the number of moles adsorbed per square centimeter and θ is the number of molecular layers, assuming the adsorbed substance possesses the same density as in the liquid state.

ETHYL ALCOHOL

Temperature 21° C.

Pressure of Gas mm. of Mercury		Surface Tension of Mercury		N	θ
P_1	P_2	γ_1	γ_2		
1.0	8.5	451	439	2.3×10^{-10}	.30
1.0	12.0	451	434	2.8×10^{-10}	.36
1.0	17.0	451	429	3.2×10^{-10}	.41
1.0	26.5	451	423	3.5×10^{-10}	.44
1.0	47.0	451	415	3.8×10^{-10}	.61
8.5	12.0	439	434	5.9×10^{-10}	.75
8.5	17.0	439	429	5.9×10^{-10}	.75
8.5	26.5	439	423	5.8×10^{-10}	.74
8.5	47.0	439	415	5.7×10^{-10}	.73
12.0	17.0	434	429	5.9×10^{-10}	.75
12.0	26.5	434	423	5.7×10^{-10}	.73
12.0	47.0	434	415	5.7×10^{-10}	.73
17.0	26.5	429	423	5.5×10^{-10}	.72
17.0	47.0	423	415	5.7×10^{-10}	.73
26.5	47.0	423	415	5.8×10^{-10}	.74

$$\Delta\gamma = NRT \ln \frac{P_2}{P_1}$$

POLY-MOLECULAR FILMS

The apparent formation of thick poly-molecular adsorbed films may be due to chemical reaction, capillary action or solution in the solid. Patrick (104) believes this to be the case, and has proved that on freshly blown glass surfaces, both toluene and water form only mono-molecular films. He also finds that condensation does not occur at the saturation point. This only proves that freshly blown glass is not wet by water (105), and does not prove that ordinary clean glass does not adsorb large quantities of water. It is well known that strongly heated or highly dried substances have peculiar properties. Trouton (106) has shown that glass, dried intensively by heating in air dried with P_2O_5 , no longer shows the ordinary adsorption curve for water at lower temperatures, The work of Carver (107) shows that toluene forms less than a mono-molecular layer on glass but he did not approach the saturation point. Some experimental work to be described later, indicates that very close to the saturation point, toluene does form an adsorbed film three or four molecules thick. This film was thin compared with all other cases investigated. Chemical action and solution of the adsorbed material in the solid surface may occur with glass but these hypotheses are not advanced to explain adsorption on metals. Adsorption on metals is attributed to capillary action, or the existence of a very large surface

compared with the apparent area. It has been shown by many series of experiments that capillary condensation can not explain the observed phenomena (108, 109). Poly-molecular adsorption om mercury can not be attributed to a large area due to irregularities in the surface (124).

There is abundant evidence of at least a transition layer near a solid surface. From a study of the optical properties of mercury Reeses (110, 111) and Haak (112, 113) conclude that on the surface of mercury in air, there exists a gaseous transition layer about five molecules thick. The photo-electric effect on platinum indicates the existence of a transition layer more than one molecule in thickness (114). By optical means the layer of air on glass is found to be 10^{-6} mm. thick(115). DeBoer has found that the adsorbed layer of iodine on calcium fluoride is about thirty molecules thick (116). Ammonium bromide on glass gives an adsorbed film three hundred molecules thick (117, 118). The capillary action of mercury (119) furnishes additional evidence of a thick film of air on glass. Cataphoresis (120) and heat transference(121) indicate the presence of thick films. Hydriodic acid is adsorbed by glass to an extent of thirty to thirty-five molecular layers (122). Carbon dioxide (123) and toluene (124) form poly-molecular films on mercury. Rinse (125, 126) has determined the vapor pressure of volatile mercury salts in the presence of glass. Films as high as five hundred molecules in thickness are formed. Numerous other investigators

have obtained similar results (127, 128, 129, 130, 131, 132, 133, 134).

While a great many explanations have been advanced which would make unnecessary assumptions concerning the formation of adsorbed films more than one molecule in thickness, very little experimental evidence has appeared which indicates their absence. The experiments of Patrick (84), mentioned above, were not conclusive, although his work has been confirmed by Catham (135). Recently Palmer (136) has determined the maximum voltage which can be obtained on placing the two wires of a coherer in contact in liquid benzene. The wires used were of platinum. His results lead him to the conclusion that even in liquid benzene only a small part of the surface of platinum is covered with an adsorbed layer of benzene. He has written numerous articles on the use of the coherer in determining adsorption and his negative results should be considered along with the many positive results.

EXPERIMENTAL WORK

Most of the experimental work to be considered later consisted of a determination of the free energy of adsorption near the saturation point of several different gases on plane solid surfaces. The results obtained for the adsorption of water on glass agree approximately with the results obtained by most of the other investigators in this field.

Ihmori (137) was the first to investigate the phenomena thoroughly, and obtained high values. Parks (138) found that heat was evolved on the addition of water to glass until the film thickness reached 134 $\mu\mu$. Katz (139) and D'Huart (140) determined the amount of water adsorbed at various relative humidities. This work was repeated with great care by McHaffie and Lenher (141, 142, 143, 144). Similar results have been obtained by others (145, 146).

Wetting and Adsorption

METHODS OF DETERMINING WETTING

The phenomenon of wetting is of great importance to many industries (147). In lithography the metals are classed as greasy or non-greasy, depending on their tendency to acquire a coating of ink. One reason why copper is not used as a printing plate is its so-called greasy nature. A method of determining wetting affinity would obviously be of value to the lithographic industry.

Many different methods have been devised for determining whether or not a solid surface is wet by a particular liquid. A surface which is wet by a liquid can be distinguished from a surface which is not wet, by the type of curve obtained on determining the vapor pressure in contact with the solid. (105) A substance adsorbed on a surface wets that surface (148). Small drops of a liquid on a surface it wets

do not increase in size. On a surface not wetted there is a growth or decrease in size (149). Since adsorption and wetting are identical, a substance which preferentially wets a surface will be preferentially adsorbed by that surface. All spontaneous processes are accompanied by a free energy decrease, and the magnitude of this decrease measures the tendency of this process to occur. If, therefore, the free energy of adsorption is measured, that substance whose adsorption is accompanied by the greatest free energy decrease will be preferentially adsorbed by the surface. Experiments to be described later, show that on the surface of glass, copper, aluminium, lead and zinc, using toluene and water, the water is preferentially adsorbed and, therefore, these surfaces are preferentially wet by water.

Preferential wetting has been determined in a qualitative way by using emulsions. If a solid powder is shaken with an emulsion of two liquids, it should go into the phase which preferentially wets the solid. In this way it is found that zinc and copper in the presence of benzene and water are preferentially wet by water (150). Bancroft, on the other hand, finds that on shaking copper and aluminium powder with kerosene and water, they go into the oil or the interface(151, 152).

Moscicki and Broder (153) have devised a method for determining the relative wetting tendency of a liquid for various metals. The theory is that at the boiling point of the adsorbed film, the liquid will cease to wet the metal.

For platinum and water this temperature is found to be 130° C.

Some solids can be pulverized by shaking in various liquids. The relative ability of a liquid to pulverize a solid in this way, is said to be a measure of the force of attraction between the solid and liquid (154).

A method in use in the floatation industry for determining the relative wetting tendency of oil and water, is one involving a determination of the adsorption of oleic acid. Various substances adsorb oleic acid from its water solution, thus changing the surface tension of the solution. The relative amounts of oleic acid (154, 156, 157) adsorbed, determine the preferential wetting of oil or water.

Bartell and Osterhoff (158, 159, 160) have recently developed a method for measuring the pressure produced when one liquid displaces another from the pores of a highly compressed powder. From their results, they calculate the adhesion tension liquid to solid. It is probable that this method only measures the interfacial tension oil-water, since under a higher pressure than that corresponding to this interfacial tension one liquid would be displaced by the other. A somewhat similar method (161) is one involving the rise of liquids in tubes of different composition. This method will only give results if the radius of the tube is of the same magnitude as the range of molecular force.

It is probable that the heat of a chemical reaction and the free energy change in the reaction bear the same re-

lation to each other that exists in the case of the heat of wetting and the free energy of adsorption. A high value of one will indicate that the other possesses a high value. Many determinations of the heat of wetting of solids by liquids have been made (162, 163). The heat of wetting of copper by various oils has been determined by Bachman and Brieger (164). They find that the addition of oleic acid and other acids increase the heat of wetting greatly. This is probably the heat of a chemical reaction, since copper reacts with oleic acid (165). These experiments indicate that the acids in linseed oil may play an important part in lithographic processes.

WETTING AND SURFACE FORCES

Wetting and surfaces forces are very closely related. The first equation connecting the surface forces of a liquid and solid in contact, is that of Young (166).

$$S_1 + S_{12} = S_2 \quad (K)$$

S_1 = surface tension of solid

S_{12} = interfacial tension

S_2 = surface tension of liquid

K = a constant or cosine of the contact angle

If the angle of contact solid-liquid is not zero, a determination of the contact angle will give the relative wetting tendency of the liquid (167). The contact angle for various organic solids and water (168, 169) has been determined.

There are many difficulties involved in a measurement of the contact angle, since the presence of small amounts of impurities or air (170) will , in some cases, prevent wetting, and thus apparently a contact angle will be formed. The reason for the failure of water to wet various solids under all conditions will be discussed in detail later.

When the angle of contact becomes zero, the quantity KS_2 is known as the adhesion tension. To determine the adhesion tension, both the surface tension and interfacial must be known. The only method of determining interfacial tension which is known, depends on the varying solubility of particles of different sizes (171). This method of determining interfacial tension was used by Hulett (172, 173) and by Jones (174) in water solutions, and by Thompson for a solid solution (175). The method is subject to a large experimental error and the results are probably only approximate.

In investigating the surface tension of solids, frictional work (176), difference of potential (177), ~~pressure~~ heat of solution (178), force of adhesion (179, 180), dissociation pressure (181), and crystal structure (182, 183) have been used. The results are still of doubtful accuracy. The surface tension can also be calculated approximately from the latent heat of evaporation, the thermal expansion, compressibility and other physical properties (147, 184), showing that these quantities probably have the same origin.

The surface tension is roughly proportional to the hardness and inversely proportional to the molecular volume (185).

WETTING AND SOLUBILITY

It is well known that liquids of increasing solubility in each other give decreasing interfacial tensions, and that at miscibility the interfacial tension becomes zero. The free energy of wetting is probably dependent on the free energy of solution. That is, substances possessing a high free energy of solution will possess a high free energy of wetting. If a solute is allowed to distribute itself between two immiscible liquids, then at any concentration the free energies of solution will be equal. The liquid in which the solute is more soluble will have dissolved a greater amount of the substance and therefore the total change in free energy will be greatest for this liquid.

WETTING AND ELECTRODE POTENTIALS

When a metal tends to go into solution, it sets up a difference of potential. This is known as the electrode potential. The liquid in which the metal has the greatest solution pressure should preferentially wet the metal, since it will be most soluble in this liquid (186). This is apparently disproved by the work of Koch (187) who finds no connection between solubility and solution tension. This is

not conclusive since no correction was made for the presence of the metal in the solution in different degrees of association. He concludes that a high voltage indicates great affinity, but since an increased voltage in the case of silver means an increased tendency to plate out, he should have reached the opposite conclusion. Some previous workers (188) have obtained values differing from those of Koch, but their work is probably in error. Baur has suggested a formula (189) in which the solution tension of the metal in a solvent is proportional to the cube of the dielectric constant. The work of Koch seems to disprove this. The electromotive force series is not the same in all liquids (190) but the variation is not great.

The standard electrode potentials of various metals have been determined in liquids other than water. If solution tension and wetting are similar, then zinc is preferentially wet by water in the system alcohol-water, since the solution tension of zinc in water is 10^8 times that in alcohol (191).

Nernst's formula for the electromotive force of a half cell has aided greatly in the progress of electrochemical theory and practice, but it is possible that it is not a complete explanation of the process. The need of a better formula led to the consideration of the influence of the solvent. Karper (192) has suggested the formula

$E = \frac{RT}{NF} \ln \frac{P_1}{P_2} - \frac{l_{12}}{NF}$, where l_{12} represents the resultant force with which both metal and water act on an ion in the neighborhood of the electrode. The other quantities have their usual significance.

Considerable experimental work (193) indicates that the potential of a cell consisting of two metal electrodes is due not only to the potential difference between metal and solution, but may arise from a contact difference in potential between the metals. If, in any modified equation for the potential of a half cell, the observed potential measures the free energy change of the reaction, it will be independent of its point of origin.

A very important modification of the Nernst equation is that of Kleeman (194) and Butler (195). If, instead of considering the heat of the reaction, we consider the free energy change occuring, the sign determines the direction of the reaction. The electrode potential will be caused by the difference between the free energy of solution of an ion in water and the free energy of formation of the ion. The free energy of formation of the ion will be the free energy of dissociation of the substance plus its free energy of ionization. This is illustrated in the following example;

$NEF = -\Delta F_1 \; -\Delta F_2 \; -(-\Delta F_3) + RT \ln \frac{a_1}{a_2}$. The last term is for a molar solution about 3000 cal. For hydrogen

the absolute electrode potential is about .22 V (196). The free energy of dissociation is $-\Delta F_1$ = 38,000cal (197). $-\Delta F_2$, the free energy of ionization (198) equals 300,000 cal. This is the heat of ionization, but since the change in entropy on ionization is small the free energy change is approximately equal to the free energy of ionization. This will be true for all substances. Substituting in the equation gives the free energy of solution of hydrogen ion in water as 340, 000 cal.

The free energy of solution will be made up of two quantities, the free energy change produced through the reaction between the ionic charge and the molecules of the liquid, and the specific attraction between the solid and the liquid. The electromotive force of a metal in a liquid will depend therefore on the first power of the dielectric constant, the number of molecules per cubic centimeter, and on the specific attractive force.

WETTING AND OVERVOLTAGE

According to the above theory the potential of a half cell is due to the difference between the free energy of adsorption of liquid and of ion. Overvoltage may be accounted for in a similar manner. Overvoltage will exist only for gases, because only in this case will there be a difference in composition between the substance deposited and the electrode. The free energy of adsorption of the liquid will be

its free energy of wetting. The maximum possible overvoltage will equal the difference between the free energy of wetting of the liquid and the free energy of adsorption of the gas being deposited. As the current decreases the overvoltage will decrease, since a smaller portion of the liquid will be replaced by gas. This will explain the observed change in overvoltage with change in current density. Because of the existence of an equilibrium point , dependent on the Boltzmann distribution law, negative overvoltages should exist. Because of the small amount of adsorption of gases on solids, the negative overvoltages would occur only at extremely low current densities and probably are not obtainable experimentally. Increased surface, since it reduces the current density, will reduce the overvoltage. Substances with a high affinity for the liquid or a low affinity for the gas evolved will give a high overvoltage. This corresponds qualitatively with observed results.

FREE ENERGY OF SOLUTION

The wettability of solid substances, their solubility, and their free energy of solution are closely related. From the above theory the free energy of solution of dissociated compounds can be calculated. The free energy of solution of a salt in water could also be calculated from the lattice energy of the crystal and the observed free energy of solution. This has been done for the heats of solution by

Born (199), Fajans (200), Rideal (201), and Butler (202). The free energy of formation of a dissociated compound in a liquid is equal to the sum of the free energies of formation of the compound, ionization, and solution. If this quantity is greater than the free energy of formation of the substance in the dry state, the substance will be soluble at the concentration for which the calculation was made. Where the substance cannot dissolve in the dissociated form, it may still dissolve in an undissociated form. Since the free energy of solution caused by the charge on an ion is a constant for each liquid, substances arranged in the order of their free energy of solution will be arranged in the order of their wettability.

Some salts will consist of one ion with a high free energy of solution, combined with an ion with a low free energy of solution. The ion with the low free energy of solution will tend to form an undissociated acid or base and escape from solution. This is observed in the case of the so-called weak acids and bases. An ion is maintained as such in solution, through the potential difference ion to liquid, produced by the charge. If the ion is large in size, the potential difference produced by a unit charge will be low and association to form colloidal particles may occur. The fatty acid salts of the alkalies illustrate this phenomenon. This theory of solution will be considered in more detail in connection with light-sensitive films.

CLEVAGE PLANES

Wetting is dependent on the surface energy of a solid. If the reduction in surface energy through the presence of a liquid, is greater than the surface energy of the liquid, then complete wetting occurs. The region near the solid surface can be considered as a region of increasing surface tension. At the surface of a solid immersed in a liquid the interfacial surface energy will equal the surface energy in the absence of the liquid minus the free energy of adsorption of a mono-molecular film. At the surface of the mono-molecular layer the surface energy will equal the surface energy of the liquid plus the free energy of adsorption of the succeeding layers. The surface energy of each succeeding layer of molecules will be determined in a similar manner. If at any point in this series, the surface tension falls below the surface tension of the pure liquid, the liquid will apparently fail to wet the solid. This phenomenon is quite familiar in the case of two liquids (203). The failure of a liquid to wet a solid is usually attributed to the presence of impurities on the surface. Many metals, after cleaning under water, are wet by water, but on drying in the air, are no longer wet by water. The amount of organic impurities which could be adsorbed by the metal during the period of drying is considerably less than a mono-molecular layer. These metals while not wet by water, adsorb large amounts of water. The effect of drying, on the wettability of a metal,

varies from metal to metal, while the amount of available impurity in the air is constant during the time required for the experiment. These facts indicate that the apparent non-wettability of many metals is caused by the existence of a plane of clevage in the water film on the metal. Since a decreased surface tension at any point will be produced by an orientation of the molecules, this phenomenon should be most pronounced in the case of substances of high dielectric constant. This is in accord with the observed phenomena.

THE REPLACEMENT OF ONE FILM BY ANOTHER

Many equations showing the rate of adsorption have been suggested (204, 205, 206). The rate at which an adsorbed film is formed is probably very high. The time required for the formation of thick films on clean metal surfaces, when these films are formed by chemical action, is only a few minutes (207). The rate of adsorption is very rapid while the velocity of adsorption or diffusion into the interior of a substance is very low (208, 209).

The rate at which one substance will replace another in an adsorbed film will depend on several factors. In gaseous films or in thin films of substances whose average life on the surface is low, there will be a rapid, complete or partial, replacement of one substance by another. A thick film may act like a perfect crystal in a dry atmosphere. A

perfect crystal will not be dehydrated in an atmosphere in which a scratched crystal will be completely dehydrated. Although thick films of one liquid can be replaced by a film of another liquid, it is well known that this rate of replacement is low (21).

A qualitative measure of replacing tendencies can be obtained by applying the Boltzmann distribution law. The relative numbers of molecules of N_1 and N_2 in a force field will be given by the expression $\frac{N_1}{N_2} = e^{\frac{E_1 - E_2}{RT}}$ if equal quantities of both substances are present in the external phase. This is the film composition which would result due to the solid surface, if the two substances were completely miscible. The solid surface can therefore create apparent immiscibility, since, if one substance is not adsorbed it will not be present at the solid surface. If the substances are less soluble in each other than the ratio obtained from the equation, the solid surface will produce increased miscibility. The value of this ratio was found, in the cases to be considered in the experimental part, to range from slightly more than one to about five. In cases such as this, adsorption from dilute solutions does not mean that the solute preferentially wets the solid. The oil adsorption experiments for determining the floatability of an ore, indicate prefemntial wetting only where the oil adsorption is very high (211). Negative adsorption shows that the ratio of solvent to solute is greater than that given by the equation.

The small value of the ratio which is obtained in all the experiments, accounts for the observed tendency of many powders to collect at the interface when they are shaken with two immiscible liquids (212). This may also explain a phenomenon noticed by Nutting (213). When silica is covered with a thin layer of water and this in turn is covered with oil, there is a noticeable accumulation of the oil on the silica.

If two immiscible liquids are brought into contact with a solid surface the limit of solubility of one in the other will, in most cases, be reached long before the relative proportion of the two present equals the amount required by the Boltzmann distribution law. Supersaturation of the liquid forming the film will produce a force opposing the force of adsorption. Adsorption ceases when these forces become equal. If this point is reached before one film has replaced the other, then replacement will not occur except at the boundary of the film. It would be a meta-stable equilibrium corresponding to the case of the perfect crystal, since rupture of the film at any point would result in the destruction of the film.

Organic Etches and Organic Light-Sensitive Substances

The most important organic etches are probably gum arabic and tannin. Both these substances are soluble in water and almost insoluble in oil. Substances such as these will therefore, if they are adsorbed by a solid, give a sur-

face which is more easily wet by water than by oil. Since gum arabic is of value in lithography, it is probably adsorbed by the printing plates. Some experiments performed in this laboratory furnish additional evidence of this adsorption (78). Many similar phenomena have been observed. Gum arabic will increase the amount of colloidal gold in the water phase of a system consisting of oil and water (212). Sulphide particles treated with gelatin or soap solution show a decreased oleic acid adsorption (214). The wettability of mercury by paraffin is increased by the addition of fatty acids (215).

A thick film of a substance such as gum arabic will be better than a thin film. It was found through experiments performed in this laboratory by Reed and Dorst (12) that through controlled light exposure, thick films of tanned gum arabic having desirable properties could be obtained on a printing plate. The properties of films on metals have not been investigated very extensively. A method of testing the hardness of varnish films has been developed by Walker and Steel (216). Some laboratory tests showed that gum arabic films are too thin to show variations dependent on the method of preparation of the film. McBain found that the tensile strength of dried gum films varies from 700 to 1600 pounds per square inch, depending on the metal surfaces between which the film is formed. Glue and gelatin films, which contain potassium bichromate, show after exposure to

light, an increased tensile strength.

A film of ammonium bichromate and gum arabic can be rendered insoluble through light action. Numerous other substances act in a similar manner to ammonium bichromate. The composition of the film is not changed greatly by exposure, as is shown by the following experiment. A bichromate, gum arabic film containing 12% of ammonium bichromate and having a total weight of ten milligrams, was exposed to the light of an arc. The volume of gas evolved was about 2×10^{-6} moles. On heating, a large amount of gas is evolved, but this is re-absorbed on cooling, indicating a high content of water in the film. The amount of gas evolved is about equal to the experimental error in the determination, but it proves that the ability of the film to retain water is changed very little.

Oxidation will occur at points at which oxidation has started. In gum arabic, either the carboxyl or alcohol group could be oxidized. There are a large number of alcohol groups present and these groups have a high affinity for water. Most of the water absorbed by a gum film will be taken up by these groups. There are a comparatively small number of carboxyl groups present and, since on solution in water, these groups ionize giving a potential difference which stabilizes the solution, the destruction of only a few of these groups would render the gum arabic insoluble in water. Since the substance becomes insoluble, but retains its hygro-

scopic properties, its insolubilization must be produced by the removal of carboxyl groups. Oxidation in solution does not result in insolubilization in many cases since oxidation proceeds until new carboxyl groups are formed and these keep the gum arabic in solution. On a metal surface very little motion of the molecules is possible. In order to obtain action at high specific points, the oxidizing agent must be present at these points. This will occur, if, on drying, a double compound is formed between the gum and bichromate at the point at which oxidation is to occur. Carboxyl groups have far more tendency to form double compounds than other groups.

EXPERIMENTAL WORK

The detail in the experimental part of this thesis consists chiefly of data on the adsorption or absorption of water and other liquids on solid surfaces. The first part of the experimental section will be devoted to the adsorption of water and other liquids on glass and various metals. The second part of the experimental section will consist of a determination of the adsorption or absorption of water by solid films on solid surfaces.

ADSORPTION ON GLASS AND METALS

The theory of the method used in determining adsorption is considered in detail by Lenher (118). The apparatus which was used consisted of a glass tube and manometer. The glass tube was cleaned with cleaning solution, followed by distilled water. It was then evacuated at 300° C., and after cooling, it was filled with a gas and then sealed. The pressure of the gas was determined by measuring the temperature of the liquid supplying the gas. The necessary agreement between observed and calculated vapor pressures at a low temperature serves as a check on this value. It was necessary to use this method of determining the original pressure, since, while the chamge in pressure could be measured with a measuring microscope to an accuracy of .01 mm. the total pressure could only ~~to~~ be measured to about .5 mm.

The temperature was measured to 0.1^{o} C. The accuracy of the method is considerably greater than the accuracy with which the solid surfaces used can be duplicated.

The adsorption of water on glass has been measured by many different investigators (141, 142, 143). For the most accurate series of investigations, an accuracy of from 5 to 10% is claimed for the average results. In the present investigation, results were obtained for the adsorption of water which checked within 20%. With metals variations in results as high as 50% were obtained, due to difficulties in reproducing surfaces. A very large error may be introduced by assuming the apparent area to be the true area. Some recent work by Rideal (220) indicates that the area of a metal may be 5 to 10 times the apparent area. The areas of the samples used in this work probably approximated the value found by him. In the work of Rideal, the surface accessible to hydrogen ions was measured. Because of capillary action all of the smaller irregularities in the surface will be filled with liquid during the adsorption experiments. The true area may therefore be two to three times the apparent area, but it is probably much less than this.

The free energy change which is measured in the experiments will be the true free energy change only if the process is reversible. If the process is reversible, the same values should be obtained on decreasing or increasing the temperature. A small amount of irreversible adsorption

was observed with metal surfaces. Adsorption is probably followed by oxidation of the metal. To obtain comparative results, readings were taken only while the film was being formed, and not while it was evaporating.

In the following tables are given the results which were obtained for the adsorption of various liquids. After each table will be given the data and equations used in calculating the results. In the tables θ equals the number of molecular layers adsorbed. The density of the substance in the adsorbed film is assumed to be equal to the density of the liquid. Therefore $\theta = \frac{\Delta P\ V(\frac{M}{S})^{2/3}\ N^{1/3}}{TRA}$,

P is the difference between the observed pressure and the pressure which would have been present if adsorption had not occurred, M is the molecular weight, S is the specific gravity, and the other quantities have their usual significance. $-\Delta F$ is the free energy of adosrption in calories and equals $RT \ln \frac{P_v}{P_o}$ where P_v equals the vapor pressure of the liquid at the temperature T and P_o is the observed pressure. The values for the vapor pressure were obtained from the International Critical Tables and are given in millimeters of mercury. The volume of the system was 21.0 cc. The area is given under each table. The temperature is given in degrees centigrade.

In addition to the data given in the following tables, some experiemnts were made using carbon tetrachloride

and 95% alcohol. With carbon tetrachloride, the high temperature correction resulted in a high experimental error. With alcohol the amount of water vapor present could not be controlled. The alcohol-water mixture showed adsorption at two different temperatures.

The metal samples used in the experiments were cleaned by washing with alcohol and ether. All of the samples except lead possessed a polished surface.

A search of the literature resulted in the discovery of only one article on the vapor pressure of pyridine over the range to be used. This article could not be obtained and for that reason the following approximate values for the vapor pressure of pyridine were used. These pressures may be in error to the extent of 1 mm., but since only pressure differences are important they are sufficiently accurate.

Temperature Degrees C.	Vapor Pressure Pyridine
20.0	17.2
19.0	16.3
18.0	15.4
17.0	14.54
16.0	13.75
15.0	13.00
14.0	12.27
13.0	11.54
12.0	10.84
11.0	10.19
10.0	9.6

Adsorption of Water on Glass

T	P_o	P_v	θ	$-\Delta F$
23.6	13.62	21.63	----	273
22.2	13.53	19.87	.6	226
21.0	13.39	18.47	2.1	188
19.9	13.30	17.26	2.8	152
19.0	13.19	16.32	3.8	124
18.2	13.09	15.52	4.8	94
17.3	12.91	14.67	6.8	74
16.7	12.74	14.12	9.0	60
16.1	12.56	13.59	11.1	46
15.5	12.33	13.09	14.1	34
15.0	12.10	12.67	18.4	27
14.5	11.80	12.27	20.7	22
13.6	11.27	11.58	27.5	16
12.8	10.73	10.99	35.7	14
11.8	10.15	10.30	43.7	8
11.0	9.66	9.77	49.4	6
24.2	13.72	22.56	----	294
23.2	13.66	21.11	.3	259
22.4	13.60	20.11	.7	230
21.4	13.49	18.92	1.8	198
20.5	13.38	18.16	2.9	178
20.0	13.30	17.36	3.7	155
19.4	13.21	16.73	4.6	138
18.3	13.01	15.62	6.1	106
17.4	12.85	14.76	8.5	82
16.6	12.64	14.04	10.9	60
16.0	12.48	13.51	13.0	46
15.1	12.02	12.76	18.8	34
14.7	11.87	12.43	20.8	27
13.8	11.40	11.73	27.0	16
12.6	10.67	10.85	36.8	10
11.0	9.63	9.76	50.5	8

Area of glass 49.0 square centimeters

Temperature correction .036 M. M. per degree

$$\theta = \frac{4 \times 10^3 \Delta P}{T}$$

Adsorption of Pyridine on Glass

T	P_o	P_v	θ	$-\Delta F$
18.4	13.58	15.76	—	—
17.4	13.52	14.71	.2	33
16.8	13.48	14.28	.7	27
16.3	13.42	14.92	1.3	17
15.8	13.23	13.56	2.1	11
15.3	13.05	13.20	5.9	3

Area of glass 49.0 square centimeters.

Temperature correction .045 M.M. per degree.

$$\theta = \frac{1.08 \times 10^4 \Delta P}{T}$$

Adsorption of Stannic Chloride on Glass

T	P_o	P_v	θ	$-\Delta F$
19.0	12.61	16.74	—	164
18.0	12.57	16.00	.3	136
17.0	12.52	15.27	1.3	115
15.4	12.42	14.10	3.1	71
14.0	12.32	13.10	6.0	35
13.0	12.20	12.39	10.6	9

Area of glass 49.0 square centimeters.

Temperature correction .036 M.M. per degree.

$$\theta = \frac{1.4 \times 10^4 \Delta P}{T}$$

Adsorption of Toluene on Glass

T	P_o	P_v	θ	$-\Delta F$
17.6	18.36	19.27	—	30
17.4	18.35	19.05	.5	23
17.2	18.33	18.83	.8	17
17.0	18.30	18.61	1.6	10
16.8	18.27	18.40	2.4	4
18.0	19.09	19.70	—	19
17.8	19.07	19.48	.5	13
17.6	19.04	19.27	1.4	7
17.4	18.97	19.05	4.0	3

Area of glass 49.0 square centimeters.

Temperature correction .054 M.M. per degree.

$$\theta = \frac{1.3 \times 10^4 \Delta P}{T}$$

Adsorption of Water on Nickel

T	P_o	P_v	θ	$-\Delta F$
34.8	17.69	—	—	—
29.2	17.15	30.40	1	344
26.5	16.72	25.97	4.5	262
24.2	16.29	22.65	7	196
23.1	15.93	21.20	10.5	168
21.6	15.39	19.35	17	134
19.9	14.78	17.43	23	97
18.8	14.28	16.28	27.5	76
17.4	13.49	14.91	37	57
16.3	12.91	13.90	42.5	42
14.8	12.01	12.63	49	28

Area of nickel 40.0 square centimeters.

Temperature correction .072 M.M. per degree.

$$\theta = \frac{4.9 \times 10^3 \Delta P}{T}$$

32.4	15.89	—	—	—
27.4	15.39	27.38	2	344
25.6	15.17	24.63	3	289
24.2	14.88	22.65	5	249
23.0	14.68	21.07	6	213
21.5	14.28	19.24	8	174
20.2	13.92	17.76	11	142
18.4	13.27	15.87	15.5	104
17.2	12.73	14.72	19.5	84
15.8	12.16	13.46	23.5	58
14.5	11.47	12.38	28.5	43
12.5	10.43	10.87	33.5	23

Area of nickel 60.0 square centimeters.

Tamperature correction .065 M.M. per degree.

$$\theta = \frac{3.27 \times 10^3 \Delta P}{T}$$

Adsorption of Toluene on Nickel

T	P_o	P_v	θ	$-\Delta F$
30.2	19.01	37.40	—	—
27.6	18.76	32.83	3	335
24.6	18.47	28.30	5.5	252
22.1	18.15	24.70	11	181
20.7	17.90	22.90	17	142
18.4	17.26	20.13	35.5	89
17.2	16.83	18.80	50	64
15.8	16.18	17.40	72	42
14.5	15.61	16.20	91	21
28.3	17.70	34.00	—	—
26.0	17.49	30.40	2	331
24.0	17.31	27.40	4	261
21.9	17.06	24.40	8.5	210
19.8	16.81	21.80	13	152
18.9	16.60	20.71	18.5	130
17.6	16.31	19.30	26	96
15.9	15.85	17.50	41	57
14.5	15.28	16.20	62	34
13.3	14.70	15.08	83	15

Area of nickel 60.0 square centimeters.

Temperature correction .072 M.M. per degree.

$$\theta = \frac{1.15 \times 10^4 \Delta P}{T}$$

Adsorption of Water on Copper

T	P_o	P_v	θ	$-\Delta F$
32.3	15.80	36.28	—	—
26.6	15.35	26.13	2	318
24.2	15.06	22.65	3.5	241
22.2	14.74	20.08	5	181
20.5	14.34	18.09	7.5	134
18.8	13.73	16.28	11.5	100
17.5	13.19	15.00	16	73
16.0	12.44	13.53	17.5	66
15.0	11.86	12.79	27	44
14.0	11.32	11.99	30	32
12.7	10.60	11.02	33	22

Area of copper 60.0 square centimeters.

Temperature correction .047 M.M. per degree.

$$\theta = \frac{3.27 \times 10^3 \Delta P}{T}$$

The results for the adsorption of water on copper varied considerably. The above data represents one of a series of experiments.

Adsorption of Toluene on Copper

T	P_o	P_v	θ	$-\Delta F$
20.0	16.61	22.00	—	164
19.0	16.55	20.82	.3	133
18.0	16.48	19.70	1.0	103
17.0	16.38	18.60	2.2	73
16.5	16.33	18.10	3.0	59
16.0	16.27	17.60	4.2	45
15.5	16.19	17.10	5.6	32
15.0	16.09	16.65	7.8	20
14.6	15.96	16.28	10.6	12
20.0	16.14	22.00	—	180
19.0	16.10	20.82	.1	143
18.0	16.04	19.70	.5	119
17.0	15.98	18.60	1.2	88
16.0	15.89	17.60	2.3	59
15.5	15.84	17.10	3.2	44
15.0	15.78	16.65	4.4	31
14.6	15.71	16.28	5.7	20
14.0	15.55	15.71	9.3	6

Area of copper 90.0 square centimeters.

Temperature correction .040 M.M. per degree.

$$\theta = \frac{7.76 \times 10^3 \Delta P}{T}$$

Adsorption of Pyridine on Copper

T	P_o	P_v	θ	$-\Delta F$
21.0	12.71	18.18	—	—
20.0	12.62	17.20	.7	181
19.0	12.53	16.30	1.6	153
18.5	12.48	15.85	2.1	139
18.0	12.42	15.40	2.7	125
17.5	12.36	14.97	3.4	110
17.0	12.30	14.54	4.1	96
16.5	12.23	14.14	5.0	84
16.0	12.16	13.75	6.1	71
15.5	12.06	13.37	7.5	60
15.0	11.95	13.00	9.1	48
14.5	11.83	12.63	11.1	37
14.0	11.70	12.27	13.2	27
13.5	11.54	11.90	15.8	18
13.0	11.36	11.54	18.8	9

Area of copper 90.0 square centimeters.

Temperature correction .045 M.M. per degree

The above results are the average of two seperate determinations.

$$\theta = \frac{5.9 \times 10^3 \Delta P}{T}$$

Adsorption of Water on Aluminium

T	P_o	P_v	θ	$-\Delta F$
38.0	15.27	49.71	—	—
36.2	15.16	45.06	1	670
33.3	14.98	38.38	1.5	585
31.5	14.80	34.68	2	509
29.7	14.65	31.29	3.5	457
27.8	14.50	28.03	4.5	393
25.2	14.21	24.05	6.5	312
23.2	13.64	21.33	10.5	264
21.3	13.12	19.02	15	218
19.7	12.68	17.22	18	179
18.5	12.32	15.97	24.5	151
16.9	11.74	14.44	29.5	119
15.6	11.21	13.29	34	96
14.6	10.78	12,46	38	83
13.5	10.32	11.61	41	67
12.4	9.84	10.80	45	53
11.4	9.35	10.11	49.5	45
10.3	8.88	9.40	52	32

Area of aluminium 60.0 square centimeters.

Temperature correction .047 M.M. per degree.

$$\theta = \frac{3.27 \times 10^3 \Delta P}{T}$$

Adsorption of Water on Aluminium

T	P_o	P_v	θ	$-\Delta F$
41.2	14.95	58.49	—	—
36.5	14.70	45.80	1	700
34.0	14.55	39.91	2	604
32.0	14.39	35.67	3.5	550
30.0	14.23	31.83	5	485
27.9	14.06	28.19	6.5	416
26.0	13.90	25.22	8	355
24.4	13.76	22.93	9.5	301
22.8	13.56	20.82	12	252
21.6	13.32	19.35	14	219
20.6	13.10	18.20	16.5	191
19.6	12.85	17.11	18	167
18.6	12.58	16.07	20	143
17.8	12.34	15.29	22.5	124
16.5	11.83	14.08	27.5	99
15.6	11.44	13.29	33.5	86
14.6	11.00	12.46	37	72
13.6	10.57	11.68	45	56
12.6	10.14	10.94	51	43
11.8	9.74	10.38	53	36
10.2	8.94	9.33	60	25

Area of aluminium 40.0 square centimeters.

Temperature correction .036 M.M. per degree.

$$\theta = \frac{4.9 \times 10^3 \Delta P}{T}$$

Adsorption of Toluene on Aluminium

T	P_o	P_v	θ	$-\Delta F$
20.9	15.39	23.17	—	—
17.4	15.17	19.02	2	117
16.2	15.06	17.80	4	96
15.5	14.99	17.12	6	76
14.5	14.87	16.20	9	49
13.9	14.80	15.65	11	29
13.3	14.66	15.08	16	16
12.7	14.44	14.60	24	6

Area of aluminium 45.0 square centimeters.

Temperature correction .050 M.M. per degree.

$$\theta = \frac{1.45 \times 10^{4} \Delta P}{T}$$

19.7	16.69	21.66	—	—
18.7	16.60	20.50	2	122
18.1	16.54	19.80	3	104
16.0	16.33	17.60	6	43
15.0	16.08	16.67	14	20
14.0	15.62	15.71	29	3

Area of aluminium 50.0 square centimeters.

Temperature correction .055 M.M. per degree.

$$\theta = \frac{1.27 \times 10^{4} \Delta P}{T}$$

Adsorption of Water on Zinc

T	P_o	P_v	θ	$-\Delta F$
41.1	15.40	58.67	—	—
37.5	15.17	48.38	3	712
36.0	15.08	44.58	3.5	667
33.0	14.77	37.74	7	570
31.2	14.59	34.09	9.5	513
29.2	14.39	30.40	11.5	452
27.3	14.23	27.22	14	388
25.5	14.01	24.48	16	331
24.2	13.91	22.65	18	287
22.6	13.69	20.57	20	239
21.0	13.36	18.66	23.5	195
19.7	13.14	17.22	25	158
18.7	12.88	16.18	27	135
17.5	12.46	15.00	31	106
15.5	11.99	13.21	33.5	55
14.4	11.47	12.30	42	41
13.0	10.68	11.23	45	24

Area of plate 35.0 square centimeters.

Temperature correction .036 M.M. per degree.

$$\theta = \frac{5.6 \times 10^3 \Delta P}{T}$$

Adsorption of Water on Zinc

T	P_o	P_v	θ	$-\Delta F$
43.3	17.18	65.33	—	—
40.6	16.99	57.13	1.5	756
39.7	16.91	54.45	2.5	725
36.0	16.48	44.58	7	610
33.4	16.34	38.60	8	530
30.5	16.12	32.76	9.5	427
28.1	15.94	28.52	11.5	353
26.8	15.49	26.43	17	318
25.2	15.24	24.05	20.5	272
22.9	14.77	20.95	25	206
21.5	14.48	19.24	27.5	166
19.6	14.01	17.11	31.5	115
18.7	13.58	16.18	36.5	99
17.4	13.26	14.91	39	65
15.8	12.68	13.46	41	34

Area of zinc 40.0 square centimeters.

Temperature correction .036 M.M. per degree.

$$\theta = \frac{4.29 \times 10^3 \Delta P}{T}$$

Adsorption of Toluene on Zinc

T	P_o	P_v	θ	$-\Delta F$
18.7	15.94	20.50	—	—
16.6	15.82	18.20	2	75
15.4	15.73	17.04	5	46
14.8	15.65	16.50	8	30
14.1	15.46	15.82	16	13
17.4	15.48	19.07	—	—
16.2	15.41	17.80	2	83
15.3	15.31	16.95	5	58
14.2	15.18	15.92	9	27
13.6	15.00	15.32	17	12

Area of zinc 37.0 square centimeters.

Temperature correction .044 M.M. per degree.

$$\theta = \frac{1.72 \times 10^4 \Delta P}{T}$$

Adsorption of Water on Silver

T	P_o	P_v	θ	$-\Delta F$
30.6	13.61	32.95	—	—
27.4	13.25	27.38	1.5	430
25.8	13.07	24.92	2	383
24.0	12.93	22.38	2.5	325
22.2	12.71	20.08	4	268
19.6	12.21	17.22	6	2000
17.9	11.78	15.38	8	154
16.7	11.46	14.26	9.5	126
15.4	11.10	13.12	12	96
14.3	10.70	12.23	14	76
13.2	10.27	11.38	15.5	59
11.7	9.66	10.31	17	36

Area of silver 80.0 square centimeters.

Temperature correction .045 M.M. per degree.

$$\theta = \frac{2.45 \times 10^3 \Delta P}{T}$$

Adsorption of Water on Silver

T	P_0	P_v	θ	$-\Delta F$
30.0	14.57	31.83	—	—
27.3	14.32	27.22	1.5	382
25.0	14.03	23.76	3	313
23.0	13.81	21.07	4	250
21.6	13.59	19.35	5	208
20.4	13.34	17.98	6.5	175
18.9	12.91	16.38	9	138
17.4	12.48	14.91	12	102
15.8	11.87	13.46	16	73
14.0	11.15	11.99	21	41
12.8	10.50	11.09	23.5	31

Area of silver 60.0 square centimeters.

Temperature correction .045 M.M. per degree.

$$\theta = \frac{3.27 \times 10^3 \Delta P}{T}$$

Adsorption of Pyridine on Silver

T	P_o	P_v	θ	$-\Delta F$
26.4	13.16	—	—	—
21.0	12.80	18.20	2.5	206
18.9	12.58	16.21	5.5	148
17.8	12.44	15.23	7.5	117
16.7	12.30	14.31	10	88
15.7	12.08	13.53	14.	65
14.5	11.76	12.63	20	41
13.3	11.33	11.76	28	21
12.1	10.65	10.91	43	14

Area of silver 80.0 square centimeters.

Temperature correction .045 M.M. per degree.

$$\theta = \frac{6.6 \times 10^3 \Delta P}{T}$$

24.0	13.90	—	—	—
22.2	13.72	19.45	2.5	206
19.5	13.47	16.75	5	127
17.8	13.29	15.23	8	79
16.8	13.11	14.39	11	53
15.6	12.71	13.45	21	32
14.6	12.28	12.71	32	25
13.7	11.78	12.05	45	13

Area of silver 60.0 square centimeters.

Temperature correction .050 M.M. per degree.

$$\theta = \frac{8.82 \times 10^3 \Delta P}{T}$$

Adsorption of Water on Lead

T	P_0	P_v	θ	$-\Delta F$
48.5	19.33	85.32	—	—
41.0	18.33	58.36	7.5	725
40.0	18.26	55.34	8	691
38.8	18.10	51.88	9.5	652
36.8	17.74	46.56	13	600
34.8	17.09	41.72	20	550
33.0	16.61	37.74	25	500
31.5	16.25	34.68	29	460
29.8	15.93	31.87	33	410
27.9	15.50	28.19	37	357
24.3	14.56	22.79	47.5	265
22.8	14.09	20.82	53	230
21.0	13.48	18.66	59	190
19.3	12.83	16.79	65	157
18.1	12.39	15.58	70	133
17.0	11.81	14.53	77.5	120
16.0	11.38	13.64	82.5	103
15.0	10.98	12.79	87	88
13.9	10.48	11.91	91.5	73
12.8	10.05	11.09	95	56
11.8	9.55	10.38	101	48
10.0	8.69	9.21	109	33

Area of lead 48.0 square centimeters.

Temperature correction .054 M.M. per degree.

$$\theta = \frac{4.08 \times 10^3 \Delta P}{T}$$

Adsorption of Water on Lead

T	P_o	P_v	θ	$-\Delta F$
48.3	19.57	85.02	—	—
43.0	18.85	64.82	8	778
40.8	18.53	57.74	12	710
38.8	18.25	51.88	16	650
36.5	17.96	45.80	18	578
33.5	17.24	38.81	30	495
31.1	16.88	33.90	34.5	423
29.5	16.59	30.93	37.5	376
27.6	16.12	27.70	46.5	324
26.7	15.94	26.28	49.5	297
24.6	15.44	23.20	56	241
23.2	15.01	21.33	63	208
22.1	14.40	19.95	73	192
20.7	14.04	18.31	79	155
19.6	13.58	17.11	86	136
18.4	13.11	13.87	92	111
17.4	12.68	14.91	100	94
16.1	12.14	13.72	107	70
15.1	11.67	12.87	113	56
13.4	10.84	11.53	121	37
12.1	10.16	10.59	127	23

Area of plate 33.0 square centimeters.

Temperature correction .054 M.M. per degree.

$$\theta = \frac{5.94 \times 10^3 \Delta P}{T}$$

Adsorption of Toluene on Lead

T	P_o	P_v	θ	$-\Delta F$
27.0	16.74	28.12	—	—
22.0	16.28	24.55	6.5	242
20.2	16.10	22.25	10	189
18.2	15.89	19.93	13.5	132
17.2	15.71	18.80	18	104
16.0	15.50	17.60	24	73
14.8	15.18	16.48	36	47
13.5	14.64	15.25	55.5	24
12.7	14.21	14.55	73	13
26.5	16.02	31.15	—	—
20.7	15.42	22.90	6	230
19.5	15.28	21.43	8.5	196
18.0	15.10	19.70	11.5	155
16.8	14.88	18.40	17	121
15.4	14.59	17.03	26	89
14.4	14.34	16.10	32.5	66
13.2	13.91	14.98	50	42
12.1	13.48	14.05	66	24
10.8	12.83	13.10	90	12

Area of lead 50.0 square centimeters.

Temperature correction .065 M.M. per degree.

$$\theta = \frac{1.28 \times 10^3 \Delta P}{T}$$

DISCUSSION OF RESULTS

The results show that glass, zinc, aluminium, lead, and copper will preferentially adsorbe water from a toluene water mixture. They also show that polymolecular adsorbed films of water and toluene are formed on these substances. If polymolecular adsorbed films exist then the internal forces in a pure liquid will produce at the liquid surface a transition film which will be similar to an adsorbed film. The formation of polymolecular adsorbed films only near the dew point shows that the influence of the solid surface has practically disappeared at the surface of a monomolecular film. Polymolecular adsorbed films therefore probably correspond to transition films on liquid surfaces.

ABSORPTION OF MOISTURE BY INSOLUBLE GUM FILMS

The plates used in the following experiments were cleaned and coated on a whirler rotating at 150 R.P.M. with a solution containing 10% solids. They were exposed at a distance of 50 centimeters to a single white flame carbon arc operating at 30 volts and 32 amperes. The humidity was measured with a hair hygrometer which had been freshly calibrated with a wet and dry bulb hygrometer. The per cent moisture absorbed is given as the per cent increase in weight of the film assuming the film weight at 30% relative humidity to be the weight of the dry film.

Table 1

Plate 1		Plate 2		Plate 3	
A	B	A	B	A	B
28	-.31	26	-.62	30	—
30	—	31	.12	31	.12
38	1.93	37	.99	36	.73
44	1.40	41	1.48	40	1.16
45	1.55	44	1.91	46	1.83
47	1.71	48	2.35	52	2.51
49	2.02	52	2.78	56	2.99
56	2.64	55	2.97	60	3.42
61	3.11	58	3.21	65	4.15
68	3.96	60	3.58	75	6.35
75	4.81	63	4.01		
77	5.11	73	4.25		
80	5.82				

A is per cent relative humidity.

B is per cent moisture absorbed.

Plate one was exposed for thirty seconds, plate two for one minute, and plate three for two minutes. The solution used in coating the plates contained 90.0% water, 9.68% gum arabic, and .32% ammonium dichromate.

Table 2

Plate 1		Plate 2		Plate 3		Plate 4	
A	B	A	B	A	B	A	B
21	-1.69	30	—	28	-.35	24	-1.44
26	— .82	35	.64	30	—	29	— .21
31	.19	40	1.40	38	1.46	35	1.03
38	1.57	48	2.67	42	2.00	40	1.72
40	2.07	52	3.17	53	3.29	47	2.27
43	2.44	56	3.68	57	3.65	52	2.68
45	2.69	60	4.19	61	4.12	58	3.23
47	3.01	66	4.70	65	4.47	67	4.19
52	3.57	80	6.22	68	4.82	74	5.02
55	3.83			75	5.65	80	6.25
60	4.20			82	7.29		
63	4.33						
75	5.33						
80	5.83						

A is per cent relative humidity.

B is per cent moisture absorbed.

Plate one was exposed for four minutes, plate two for two minutes, plate three for one minute, and plate four for thirty seconds. The solution used in coating the plates contained 90.0% water, 9.37% gum arabic, and .63% ammonium dichromate.

Table 3

Time of exposure	1'	2'	4'	8'
A	174	83	83	81
B	90	80	79	81
C	83	80	74	66
D	79	80	68	63

The above table gives the per cent moisture absorbed at 100% relative humidity by different plates exposed for the time given in the table. Plates A were coated with a solution containing 90.0% water, 9.68% gum arabic, and .32% ammonium dichromate, plates B with a solution containing 90.0% water, 9.37% gum arabic, and .63% ammonium dichromate, plates C with a solution containing 90.0% water, [illegible].90% ammonium dichromate, and 9.10% gum arabic, and plates D with a solution containing 90.0% water, 8.25% gum arabic, and 1.65% ammonium dichromate. The plates were allowed to stand in the relative humidity cabinet for several days before they were weighed. The high result obtained for plate A after one minute exposure is probably incorrect since about 90% of the film was removed on washing.

SUMMARY

Each process involved in the production and use of a printing plate has been studied, and a possible theory for the observed phenomena has been suggested. Adsorption and wetting, which are considered as related, are found to be important in the action of etches and in the slow change in size of the image. Adsorption, which results in mono-molecular films, is shown to be of only secondary importance in lithography. Of the various attractive forces which produce adsorption, the Van der Waals force is the only one which produces thick films. This force is shown to depend on the mass and volume of the atom or molecule, as well as on the kind of bond present. The values given in the literature for the magnitude and rate of decrease of this force vary over a wide range. The results obtained in this thesis show, that as the force changes from 10^{-11} dynes to 10^{-13} dynes, the rate of decrease is approximately proportional to the inverse first power of the distance.

Matter is composed of particles and therefore the surface of a solid consists of points of attraction. The adsorbed material on a surface may be concentrated at these points of attraction or distributed more uniformly over the surface. The adsorption theory of Langmuir, which is based on the discrete nature of matter is applied to a lithographic problem. Some experimental evidence is advanced which shows that the theory may not be of importance in lithography.

When adsorption is localized at points on a surface the electrical properties of the adsorbed substance may be of paramount importance. The dipole theory of adsorption is applied to inorganic etches. According to this theory an inorganic etch consists of a substance which is adsorbed by the metal and whose surface consists of a distribution of ionic charges, similar to the surface of a crystal of sodium chloride.

The various evidence to be found in the literature concerning the existence of a thick, diffuse, adsorbed film, is discussed. The free energy of adsorption, wetting affinity, and the Gibbs adsorption isotherm are shown to be identical. This equation is applied to the experimental data of Iredale. The results show that the equation can be applied to adsorption on metals over the entire range of pressure and up to the condensation point of a vapor. Evidence against this theory is considered and shown to be inconclusive. The free energy of adsorption of water and toluene on glass, copper, zinc, aluminium, nickel, lead and silver has been determined. The results show that glass, copper, zinc, aluminium and lead, are preferentially wet by water in the presence of water and toluene.

The ability of one substance to replace another on a solid surface and the rate at which this can occur, are discussed. The Boltzman distribution law is considered in relation to the displacement of one liquid by another in which it is insoluble. The results obtained show that the forces

of adsorption can cause replacement only at the edge of an adsorbed film.

The various methods of determining wetting which have been proposed, are considered in detail. It is shown that the free energy of adsorption and of wetting equals the change in surface energy which is produced. The various methods of determining the surface tension of solids are discussed. A relation between wetting and solubility is pointed out. The liquid in which the solid is more soluble, preferentially wets the solid. A tendency to dissolve, in the case of metals, is known as solution tension. The electrode potentials of a metal in different liquids therefore, are a measure of the tendency of these liquids to wet the metal.

The formation of insoluble gum arabic films is considered from a theoretical standpoint, and the mechanism proposed is shown to agree with various experimental facts. The amount of moisture absorbed by tanned gum arabic was determined for different times of exposure, at various relative humidities.

CONCLUSION

The tendency of an image on a lithographic plate is to increase in size. To prevent this, etches are used. They can prevent this increase in most cases, but cannot reverse this action unless they contain inorganic acids. The tendency of the image to grow in size is accelerated by the presence of substances causing an increased solubility of ink in water, and by the presence of organic acids. The values obtained for the wetting tendency of toluene and water on various metals, indicate that no possible bi-metallic combination can entirely overcome the tendency of the image to spread.

The use of an organic film obtained by light action gives to the non-printing portions of the plate, properties not obtainable from bi-metallic combinations. The properties of the film change gradually on light exposure and there is no abrupt change from water to oil absorbing properties.

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216. Sci.Sec.Paint Varnish Manuf.Assoc.----Walker and Steele
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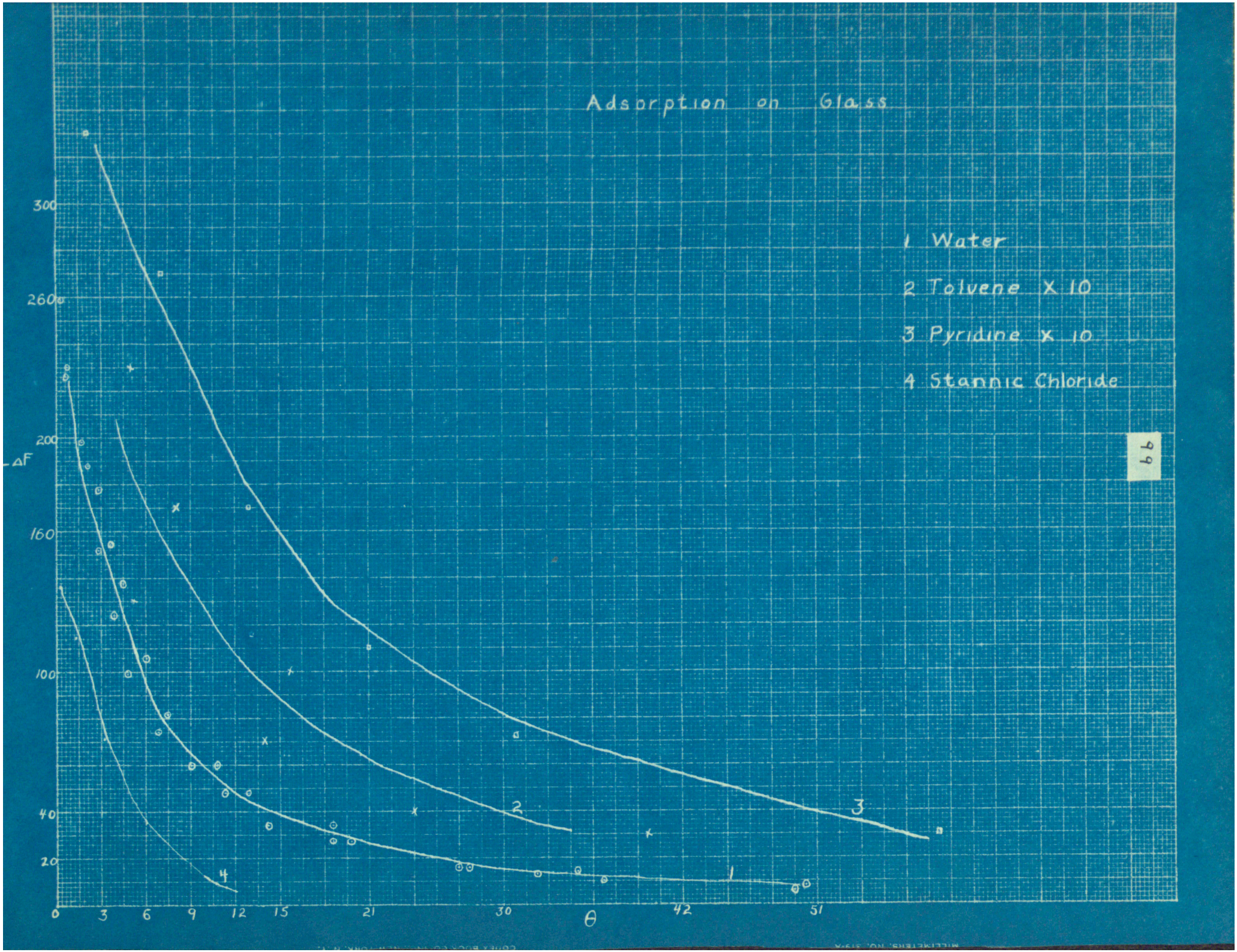
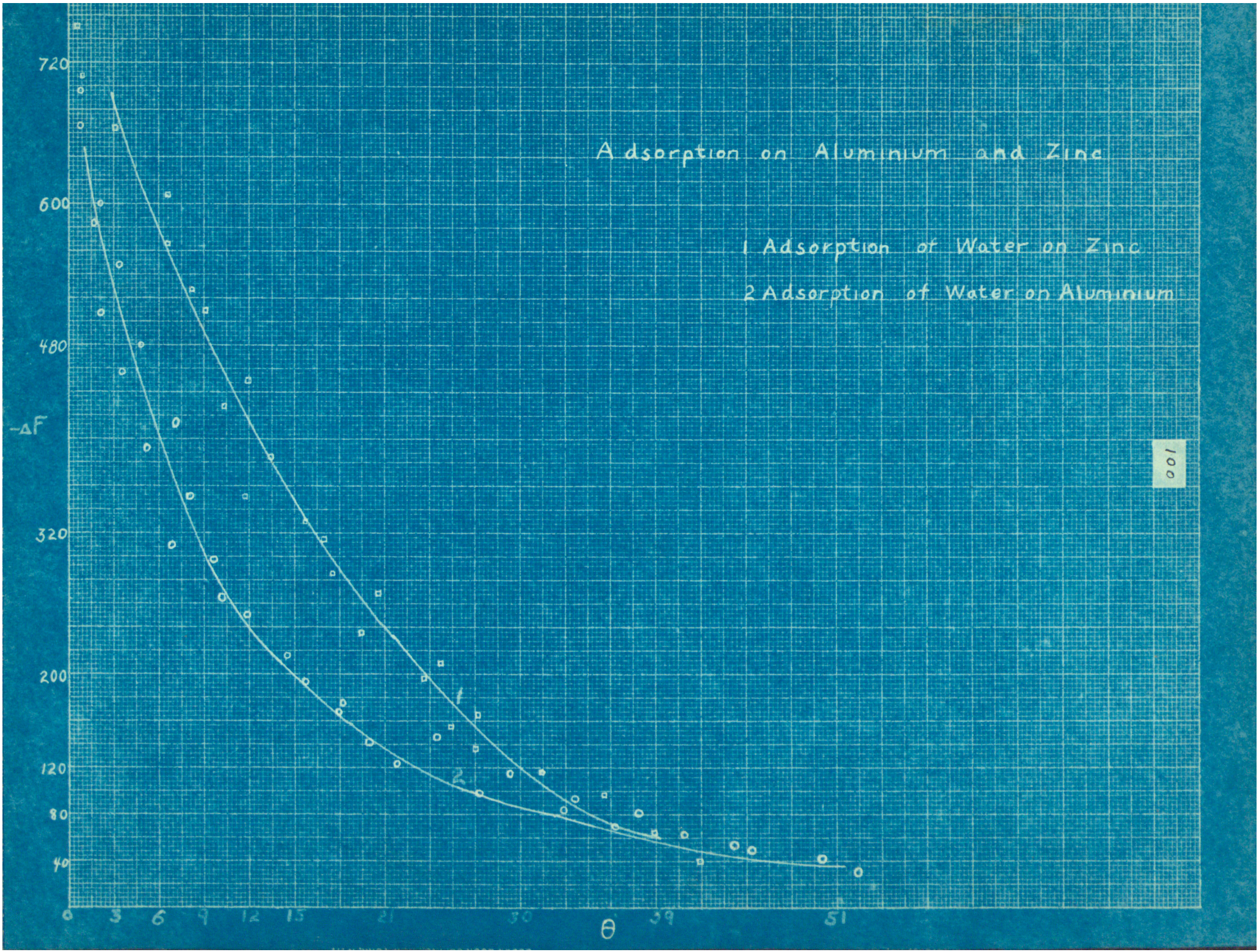
217. J.Phys.Chem., V.29, p.188--------McBain and Hopkins

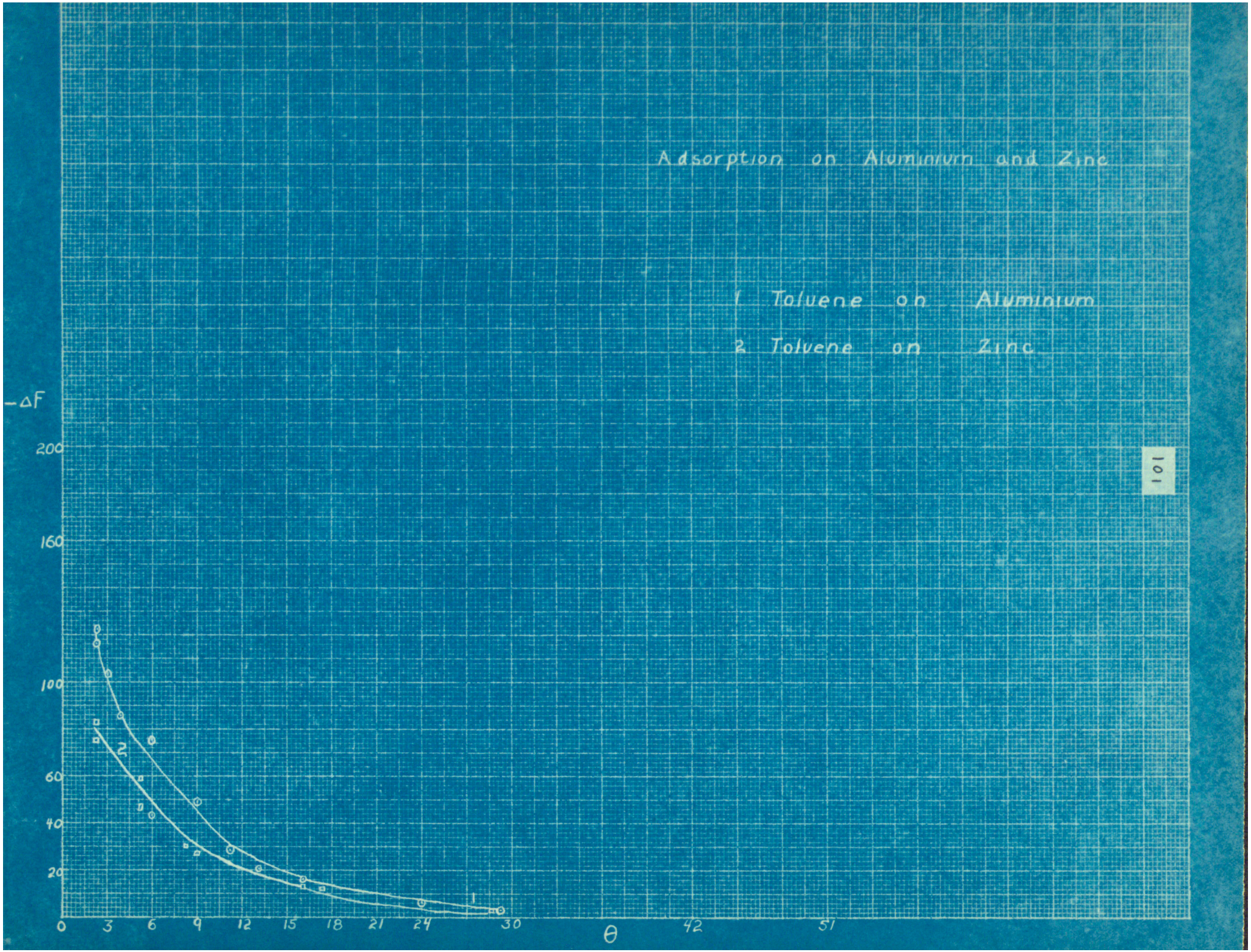
218. J.Soc.Chem.Ind., V.46, p.321-----McBain and Hopkins

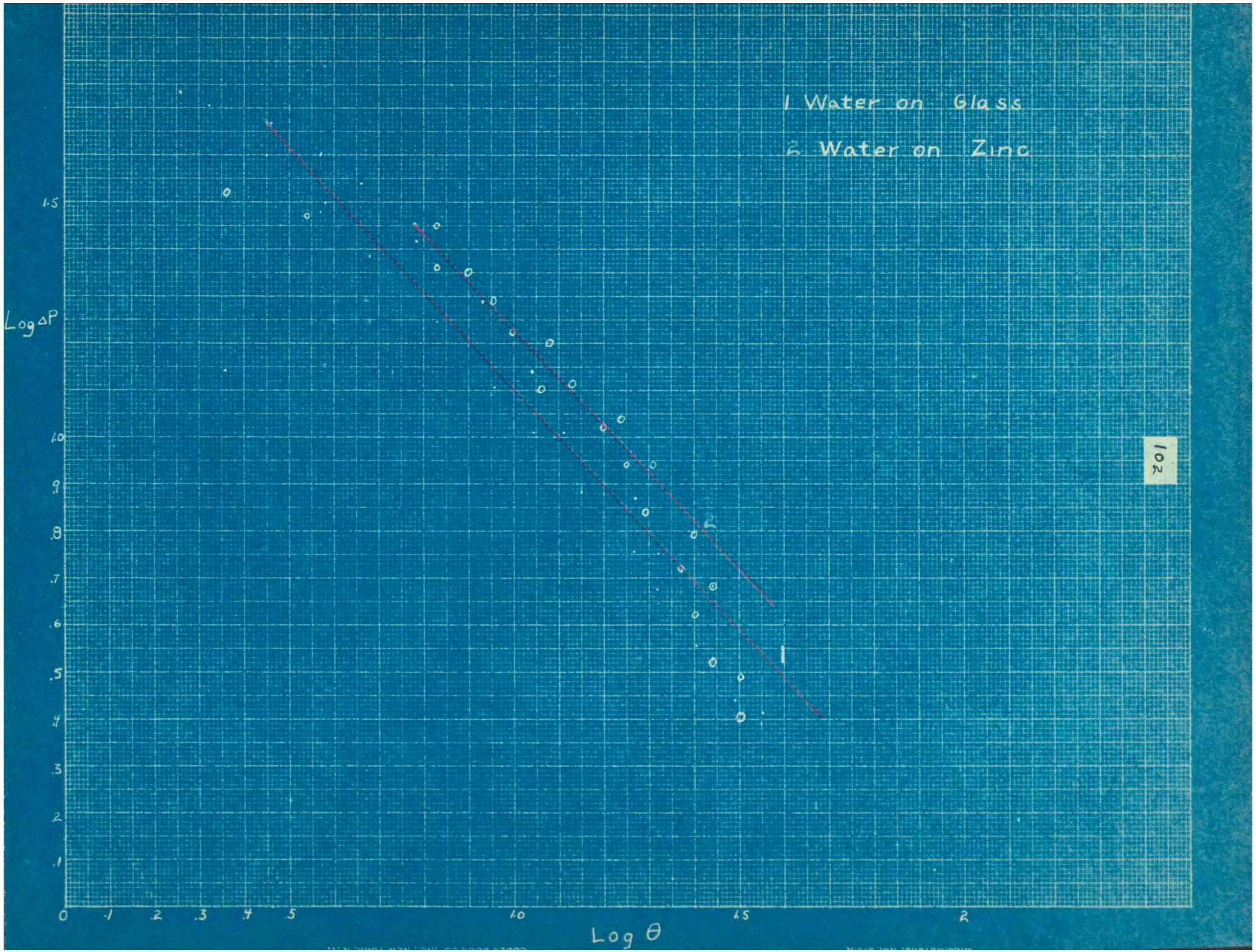
219. J.Ind.Eng.Chem., V.19, p.1005 ----McBain and Lee

220. Proc.Royal Soc., V.120, p.80-----Rideal and Bowden


Adsorption on Glass
1 Water
2 Tolvene X 10
3 Pyridine X 10
4 Stannic Chloride
99
300
260
200
160
100
40
20
-ΔF
0
3
6
9
12
15
21
30
42
51
θ
1
2
3
4


Adsorption on Aluminum and Zinc
1 Adsorption of Water on Zinc
2 Adsorption of Water on Aluminium
720
600
480
-ΔF
320
200
120
80
40
0
3
6
9
12
15
21
30
39
51
θ
100


Adsorption on Aluminium and Zinc
1 Toluene on Aluminium
2 Toluene on Zinc
101
−ΔF
200
160
100
60
40
20
0
3
6
9
12
15
18
21
24
30
θ
42
51
1
2


1 Water on Glass
6 Water on Zinc
Log ΔP
1.5
1.0
.9
.8
.7
.6
.5
.4
.3
.2
.1
0
.1
.2
.3
.4
.5
1.0
1.5
2
Log θ