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FUGACITY AND CONCENTRATION GRADIENTS IN A GRAVITY FIELD

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SUMMARY

Equations are reviewed which show that at equilibrium fugacity and concentration gradients can exist in gravitational fields. At equilibrium, the logarithm of the ratio of the fugacities of a species at two different locations in a gravitational field is proportional to the difference in the heights of the two locations and the molecular weight of the species. An analogous relation holds for the concentration ratios in a multicomponent system. The ratio is calculated for a variety of examples. The kinetics for the general process are derived, and the time required to approach equilibrium is calculated for several systems. The following special topics are discussed: ionic solutions, polymers, multiphase systems, hydrostatic pressure, osmotic pressure, and solubility gradients in a gravity field.

INTRODUCTION

Application of the relationship that exists between fugacity and position in a gravity field might lead to a better understanding of the behavior of both living and nonliving matter in a gravity field. For instance, this relationship might be involved in the mechanism by which the roots of a plant are directed downward. Eventually, the resultant knowledge may suggest micro-gravity experiments that will add still more to the understanding of gravity.

Consider a material in a gravitational field. The upper portion of the material has a higher gravitational potential energy than the lower portion. Of course, the difference is small compared with most other effects. In zero gravity this effect does not exist, and all parts of a material have the same potential energy. The existence of a gravitational potential gradient can affect the behavior of materials.

Sometimes, this fact is not recognized even though the effect was treated years ago by Guggenheim (ref. 1) and others. Guggenheim began with the following equation.

$$d(\mu_i + M_i \varphi) = 0 \quad (1)$$

where μ is the chemical potential; φ is the gravitational potential; and i refers to the i 'th species in a solution. Equation (1) ignores contributions from surfaces and fields other than gravitational. Via equation (1) Guggenheim expressed the change in mole fraction, N_i , of a species in an ideal solution as a function of the change in gravitational potential.

$$RT \, d \log N_i + \left\{ M_i - \bar{V}_i \frac{\sum (N_k M_k)}{\sum (N_k \bar{V}_k)} \right\} d\varphi = 0 \quad (2)$$

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where M refers to molecular weight; \bar{V} , to partial molal volume; $\sum(N_k M_k)$ is the effective molecular weight of a mole of the solution; and $\sum(N_k \bar{V}_k)$ is the volume of a mole of solution. The ratio, $\sum(N_k M_k)/\sum(N_k \bar{V}_k)$, equals the density of solution, ρ . Koenig (ref. 2) extended Guggenheim's equation to apply to nonideal solution. More recently Guggenheim (ref. 3) has expressed the fugacity of species in a mixture of perfect gases as a function of position in a gravitational field.

$$\frac{dp_i}{p_i} = - \left(\frac{M_i}{RT} \right) d\varphi \quad (3)$$

where p is the fugacity (idealized pressure); and M , the molecular weight. Guggenheim's equations are difficult to apply in the form they are given. Because a single phase is sometimes defined as a system of uniform composition, and a gravitation field requires a nonuniform composition at equilibrium, Guggenheim refers to an equilibrium system in a gravitational field as a multiphase system. Thus, by his definition, an equilibrium aqueous solution of sodium chloride in the earth gravitational field should be referred to as a multiphase system. Such terminology is confusing and, therefore, is not used in this report.

In the case of an ideal gas, the equations that have been derived are in a more usable form (ref. 4)

$$\ln \frac{P}{P_0} = \frac{-Mg(h - h_0)}{RT} \quad (4)$$

where P is the pressure of the gas at the higher altitude h ; P_0 is the pressure at the altitude h_0 ; M is the molecular weight; g is the acceleration of gravity; R is the gas constant; and T is the absolute temperature. Equation (4) can be derived in several ways, independently of Guggenheim's equations. In a mixture of gases, each component obeys equation (4) individually where M , P , and P_0 refer to the same component. The concentration gradient in the earth's atmosphere is due at least in part to the relationship expressed in equation (4). Equation (4) also applies to the separation of isotopic gaseous species under the high gravity conditions of a centrifuge.

In 1908, Perrin (ref. 5) modified equation (4) in order to apply it to a suspension of particles in a liquid.

$$\frac{RT}{N} \ln \frac{n_0}{n} = \frac{4}{3} \pi r^3 gh(\rho - \rho') \quad (5)$$

where r is the radius of the particles; N is Avogadro's number; ρ' is the density of a particle; ρ is that of the liquid; n and n_0 refer to the concentration of the particles at two different heights; and h is the difference in their heights. From experimental data and equation (5), Perrin calculated Avogadro's number to about a 15 percent accuracy. His experiments validated equation (5). Since then, however, it has been shown that equation (5) holds only in a relative narrow range of h (ref. 6).

Block et al. (ref. 7) have found concentration gradients to occur in gravitational fields in excess of 10^5 times normal gravity for a liquid solution several degrees above its liquid - liquid critical solution point. The solution was a mixture of n-hexane and perfluoro-n-hexane. Similarly, Moldover et al. (ref. 8) have reported density gradients to exist in gravity fields for systems near their gas - liquid critical point. Other investigators have shown similar results.

Diffusion kinetics for the attainment of concentration equilibrium in a gravitational field appears to be lacking from the literature although diffusion of ions in an electrical field has been treated (ref. 9).

The purpose of this report is to present the appropriate equilibrium equations in usable forms, to apply them first to simple examples, to derive the applicable kinetic equations, to evaluate the time required for approach to equilibrium, and finally to apply the equilibrium equations to certain special cases such as ionic solutions and osmotic pressure.

EQUILIBRIUM EQUATIONS AND CALCULATIONS

In the first part of this report, our attention is directed toward only single phases in a uniform gravitational field. We define h_1 as a distance between the gravitational source and some position in the phase and h_2 as the distance between another position in phase and the gravitational source. If the difference between these values, h , is small with respect to the values themselves, the gravitational potential may be expressed as a linear function of h . In differential form the relationship becomes:

$$d\phi = -g dh \quad (6)$$

where g is the acceleration of gravity, and h is measured toward the gravitational source.

Concentration

To make equation (2) more usable in predicting concentration gradients in the condensed state, equation (6) is used to express the gravitational potential difference. Combining equations (2) and (6) yields:

$$RT d \ln(N_1) = \frac{RT dN_1}{N_1} = (M_1 - \bar{V}_1 \rho) g dh \quad (7)$$

If j refers to the solvent, $dN_j = -\sum dN_i$. Combining this equation with equation (7),

$$RT dN_j = -\left\{ \sum N_i (M_i - \bar{V}_i \rho) \right\} g dh \quad (8)$$

Moreover, the average molecular weight of the solution, $M = N_j M_j + \sum (N_i M_i)$; the volume of a mole of solution, $V = N_j \bar{V}_j + \sum (N_i \bar{V}_i)$; and $M = \bar{V} \rho$. Thus $\sum \{N_i (M_i - \bar{V}_i \rho)\} = -N_j (M_j - \bar{V}_j \rho)$. Combining this equation with equation (8),

$$\frac{RT dN_j}{N_j} = (M_j - \bar{V}_j \rho) g dh \quad (9)$$

Equation (9) states that if all the solutes obey equation (7), the solvent obeys the same relationship.

Equation (7) can be integrated if ρ is assumed to be constant. This assumption is only valid for a dilute noncompressible solution.

$$RT \ln \left(\frac{N_j''}{N_j'} \right) = gh(M_j - \bar{V}_j \rho) = gh(V_j \rho_j - \bar{V}_j \rho) = ghB_j \quad (10)$$

where \bar{V}_j is the partial molal volume of species j in solution; V_j is the molar volume of pure species j ; and ρ_j is its density. Equation (10) is completely valid for the solute in a dilute ideal noncompressible solutions when the distance to the gravity source is large. The product, $\bar{V}_j \rho$, is the weight of solution corresponding to a molal volume of species j . The mass difference, $M_j - \bar{V}_j \rho$, corresponds to a buoyancy factor, B_j . When a species has a positive buoyancy factor, the species can be said to be more dense than the solution so that at equilibrium the concentration (mole fraction) of the species will be greater at the bottom than at the top. When a solute has a negative buoyancy factor, its concentration at equilibrium will be greater at the top than at the bottom.

The term ideal system (or perfectly ideal solution) is generally taken to mean that both the solvent and solute behave ideally; Raoult's law is obeyed. In this case, \bar{V}_j is equal to the molar volume of the pure species because \bar{V}_j will not be a function of concentration. Thus,

$$RT \ln \left(\frac{N_j''}{N_j'} \right) = M_j \left(1 - \frac{\rho}{\rho_j} \right) gh \quad (11)$$

where j can refer again only to a solute. The examples of truly ideal systems are rare.

In general, one must be satisfied with the treatment of "ideal solutions" in which the solutes obey only Henry's law. Henry's law requires that \bar{V}_j does not vary with concentration in the low concentration region. Outside this region equation (10) should be considered to be only an approximation; the value to be used for \bar{V}_j outside the low concentration region should likely be the value of \bar{V}_j for the concentration of interest.

It should be noted that equation (10) does not predict a constant concentration gradient throughout a column of material in a gravitational field. As a result the equilibrium concentration at midheight, in general, is not equal to the initial concentration, $N_{j,0}$. The value of the midheight concentration, $N_{j,m}$, is dependent upon the variation of the cross section of the column with height as well as on the other gravitational parameters. To derive an expression for $N_{j,m}$, we have assumed a uniform cross section. In a dilute solution, the average concentration which is equal to $N_{j,0}$ may be set equal to

$\int(N_i dx)/h$, where X is the distance measured from the top, and N_i is the corresponding concentration. The variable, N_i , may be replaced by $N_i^i \exp\{(M_i - \bar{V}_i \rho)gX/RT\}$, where N_i^i is the mole fraction at the top. Integration, rearrangement, and substitution yield:

$$\frac{N_i^i}{N_{i,0}^i} = \frac{(M_i - \bar{V}_i \rho)gh}{RT \left[\exp \frac{(M_i - \bar{V}_i \rho)gh}{RT} - 1 \right]} = \frac{\ln \left(\frac{N_i^u}{N_i^i} \right)}{\left(\frac{N_i^u}{N_i^i} - 1 \right)} \quad (12)$$

From equation (10) it can be shown that $N_{i,m}$ equals $\text{sqr}(N_i^u \cdot N_i^i)$. Introducing this into equation (12) yields:

$$\frac{N_{i,m}}{N_{i,0}^i} = \frac{\ln \left(\frac{N_i^u}{N_i^i} \right)}{\text{sqr} \left(\frac{N_i^u}{N_i^i} \right) - \text{sqr} \left(\frac{N_i^i}{N_i^u} \right)} \quad (13)$$

In figure 1, the ratio $N_{i,m}/N_{i,0}^i$ is plotted as a function of N_i^u/N_i^i . The midheight concentration is less than the initial concentration, both when the ratio N_i^u/N_i^i is greater than unity (positive buoyancy factor) and when it is less than unity (negative buoyancy factor). When N_i^u/N_i^i approaches unity (corresponding to a small product of g , h , and the buoyancy factor), $N_{i,m}/N_{i,0}^i$ also approaches unity. The fact that $N_{i,m}$ is not equal to $N_{i,0}^i$ for a solution in a gravitational field means that its center of mass is not at its geometric center.

Application to Salts

A question arises when applying the equations just derived to ionized salts. Should one treat the salt or the ion as the solute species? Equation (1) which is the starting point of the derivation is for a single species. However, when the species is an ion, it must be modified to include and the electrical potential, Z_i : $d(\mu_i + \rho_i + Z_i) = 0$. To derive a usable equation from this modified equation, Z_i must be eliminated by adding together the equations for all the species in a molecule of the salt. From such a composite equation, an equation similar to equation (7) can be derived.

$$RTd \ln(N_i) = \frac{RT dN_i}{N_i} = \frac{(M_s - \bar{V}_s \rho)g dh}{Y} \quad (14)$$

where Y is the total number of ions present in a molecule; s refers to the salt; and i can refer to either the cation or the anion. The i can also refer to the salt in the sense that the concentration of the 'ionized' salt must vary with the concentration of the anion and the cation. Remember, however, that the concentration of the 'nonionized' salt species itself is zero because we assumed a completely ionized salt. However if some of the salt were nonionized, that component of the salt would obey equation (10).

Equation (14) applies only when a single salt is present in the solution. The problem of the presence of more than one salt is treated in a later section. By the comparison of equations (10) and (14) one sees that the buoyancy factor for an ionized salt, B_s , is $(M_s - \bar{V}_s \rho)/Y$. Thus equation (10) is applicable to an ionized salt if the proper buoyancy factor is used.

Fugacity

A gravitation field also gives rise to a fugacity gradient in a column of material. This gradient may be looked upon as a combination of two effects: the concentration gradient just discussed and the hydrostatic pressure of the column itself. The effect of pressure on fugacity is well known (ref. 10).

$$RT \ln \left(\frac{f_1''}{f_1'} \right) = P \bar{V}_1$$

or more precisely,

$$RT \frac{d \ln(f_1)}{dP} = \bar{V}_1 \quad (15)$$

where f_1' is the fugacity of species 1 without the applied pressure, P ; f_1'' is its fugacity with the applied pressure; and \bar{V}_1 is the partial molal volume of the species. Because the hydrostatic pressure is equal ρgh , equation (15) can be written as follows:

$$RT \frac{d \ln(f_{1,0})}{dh} = \bar{V}_1 \rho g \quad (16)$$

where the subscript 0 indicates the condition of homogeneous composition. Thus even without a concentration gradient, a fugacity gradient exists in a column of material in a gravitational field. This equation applies to both the major and minor components (solvents and solutes).

Because Henry's law is assumed, the ratio, f_1/N_1 , is a constant for an nonionized material at any specified position in the column, and $f_1/N_1 = f_{1,0}/N_{1,0}$, f_1 being the equilibrium value of the fugacity. For an ionized salt $f_s/N_1 Y = f_{s,0}/N_{1,0} Y$. Because $N_{1,0}$ is not a function of h , one may write

$$\frac{d \ln(f_s)}{dh} = \frac{d \ln(f_{s,0})}{dh} + \frac{Y d \ln(N_1)}{dh} \quad (17)$$

For an nonionized material, the s subscripts become i 's and the Y becomes one. Combining equations (7), (16), and (17) yields

$$RT \frac{d \ln(f_i)}{dh} = M_i g$$

or

$$RT \ln \left(\frac{f_1''}{f_1'} \right) = M_1 gh \quad (18)$$

where f_1' is the equilibrium fugacity value for species 1 at the top of the column, and f_1'' is its equilibrium value at the bottom. The integration step requires g to be constant. Equation (18) holds for liquids, solids (including ionized salts), gases, solutes and even solvents. Moreover, because equation (18) does not specify properties of the solution, it holds even though Henry's law is not obeyed.

Equation (18) as applied to gases may also be derived by combining equations (3) and (6). For an ideal gas, one may also substitute pressures for fugacities and thus derive equation (4). Thus, in a mixture of ideal gases, equation (4) will apply individually to each component. Of course, when a gas or gas mixture deviates from ideality, equation (4) can still be used as an approximation.

Numerical Evaluation

Calculation of a concentration gradient expected in a gravitational field at equilibrium requires the knowledge of \bar{V}_1 of the solute. This value is calculable from the variation of density of a solution with concentration.

$$\bar{V}_1 = \frac{\frac{(100 - p_1')}{\rho''} - \frac{(100 - p_1'')}{\rho'}}{p_1'' - p_1'} M_1 \quad (19)$$

where ρ' is the density of a solution containing p_1' weight percent of solute 1; ρ'' , the density of a solution containing p_1'' weight percent of the solute; and M_1 , the molecular weight of the solute. Equation (19) is approximate but becomes precise in the limit where p_1' approaches p_1'' .

The required density data as a function of concentration are available from a variety of sources (e.g., aqueous solutions from ref. 11). Via such data and equation (19), we have calculated the values of \bar{V}_1 and thereby the buoyancy factors for a variety of solutes in water. These are listed in table I. The molecular weight used for a solute is that of its anhydrous form. The value of Y (number of species per molecule) that was used is listed in the second column. For nonionic materials, Y is one. For sodium sulfate which is a completely ionized salt, Y is three (two sodium ions and one sulfate ion). The concentration ratios given for it in table I are therefore those for the ions. For sodium chloride, also completely ionized, Y is two (one sodium ion and one chloride ion). For only slightly ionized materials such as acetic acid, ammonium hydroxide, and phosphoric acid, the value of Y given in table I is one; therefore, the concentration ratios given refer to those of the nonionized species which is the major component. Trichloroacetic acid is somewhat of a special case because it is almost but not completely ionized; in this case, the value used for Y is two. It is interesting to note that at infinite dilution, a partially ionized material would become completely ionized, and the Y to be used would be that of the completely ionized

material. Under such consideration, the value of Y for acetic acid would be two, and the concentration ratios would refer to those of the ions. However, the Y 's used in table I are ones of practical interest, those for 'reasonably' dilute solutions for which such materials are essentially not ionized.

Selection of Parameters

At equilibrium, concentration gradients are not found under normal gravity conditions. Only when large values of h (ref. 4) or large values of g are involved (refs. 7 and 8), have concentration gradients been observed. The three sets of parameters used in this report were selected in order to encompass the conditions where the gravitational effect is expected to be detected and where it is not. Parameters 'a' are 1 G (i.e., $g = 980 \text{ cm/sec}^2$) and a 1 m high column; parameters 'b' are 100 000 G's and a 1 cm high column; and parameters 'c' are a 10 000 m column at 1 G. This height approximates the depth of the 5 mile ocean. Because the gravitational concentration effect is dependent on the product of g and h (eq. (10)), ratio c is also valid for one million G's and $h = 1 \text{ cm}$. In table I the ratios of the lower to upper concentrations are given for these three sets of gravitational parameters. Equation (10) was used to make the calculations.

Examination of table I shows that the concentration ratios 'a' (corresponding to parameters a) are generally very close to unity; this is in accord with observations under normal conditions (a relatively small value for the product of g and h .) Calculated concentration differences between the top and bottom are in most cases less than one part per thousand. Only in the case of high molecular weight material (e.g., dextran) does the calculated ratio (1.122) depart significantly from unity.

Ultracentrifuge Conditions

In contrast to concentration ratios close to unity, table I shows that a considerable number of concentration ratios 'b' (for 100 000 G's and a 1 cm high column of solution: ultracentrifuge conditions) are greater than 1.1. This corresponds to concentration differences from top to bottom of more than 10 percent. Thus, concentration gradients of many dissolved materials should be measurable under ultracentrifuge conditions. There are several extreme examples in table I. One is the ratio for lead nitrate, 307, which means a concentration gradient of over 30 000 percent. It would appear from table I that the ratio is greatest for high molecular weight materials, e.g., polymers. The ratio for dextran is greater than 10^{38} ; the ratio for inulin, 2767. As discussed earlier, when the buoyancy factor is negative, the concentration of the solute at the top of a column is greater than at the bottom. This is demonstrated in the case of the organic liquids: acetone, ethanol, and methanol. Ammonium hydroxide also has a negative buoyancy factor.

Effect in Ocean

The concentration ratios 'c' in table I (for 1 G and a 10 000 m deep ocean) deviate even more from unity than the concentration ratios b. Many of the concentration ratios 'c' are greater than 10. This would imply that at equilibrium, many dissolved materials should tend to concentrate at the bottom

of the ocean and lead to the purification of its surface regions. For instance, sugars such as glucose would be about 15 times more concentrated at the ocean's bottom than at its surface. The ratio for copper sulfate is over 26, meaning that at equilibrium a copper salt dissolved in the ocean water would tend to concentrate at the bottom, leaving a much lower concentration near the surface. In contrast, the ratio for sodium chloride is only about 2.2 which means that the concentration of this salt near the surface would be comparable with its concentration near the bottom. When more than one salt exists in solution, equation (10) is not completely valid because the ions which compose the individual salts can interact. This topic is discussed later in more detail.

Higher Concentrations and Fugacities

Also included in table I is a 'range' column which is the percentage range in which the partial molal volume of the solute varies only 1 percent. For many salts this is only up to 0.5 or 1.5 percent. However, for many organic materials, the range extends to 10 percent. Acetic acid extends to 30 percent; fructose and methanol extend to over 50 percent. For this range of concentrations, the concentration ratios d were calculated assuming a constant average density and the parameters of 100 000 G's and $h = 1$ cm. In general, the ratio d does not vary more than about 1 percent from the corresponding ratio b . The greatest variation, about 5 percent, is for fructose; but this is for the concentration range up to 52 percent. The final column in table I gives the equilibrium fugacity ratio for 100 000 G's and a 1 cm high column.

Nonaqueous Systems

Equation (10) may, of course, be applied to nonaqueous solutions. This has been done in table II using data in reference 12. Table II gives the partial molal volumes of solutes in the indicated solvents, the concentration ratios for particular values of h and G , and the fugacity ratios. (The fugacity ratio of a particular species is independent of the solvent.) In the first part of table II one can find data for organic solvents, while the last part gives data for some metals. Again for the condition $h = 100$ cm and normal gravity, the concentration ratios are very close to unity. However, in a few cases, the difference between the top and bottom concentrations may exceed 0.1 percent; for example, the ratio a for tin in gold is 0.9988.

In general, ratios b in table II ($h = 1$ cm and 100 000 G's) just as those in table I deviate noticeably from unity. The exceptions are aluminum in magnesium and iron in copper. Again for solutes with high molecular weights (e.g., tristearin) the ratios b are unusually large. For many alloys, the ratios are less than unity because the corresponding buoyancy factors are negative.

One of the first solutes listed in table II is sodium nitrate. Its ratio data in methylamine can be compared with its ratio data in water given in table I. Its calculated ratio b is 1.122 in water while it is 136 in methylamine. This large calculated value in methylamine is the result of an apparent large negative value used for its partial molal volume.

In reference 12, the density of the tristearin - bromocamphor system is given over its entire composition range. This allowed two sets of calculations to be made: one where the tristearin is assumed to be the solvent and one where the bromocamphor is taken as the solvent. The calculations show bromocamphor to have a positive buoyancy factor when assumed to be the solute, and the tristearin to have a negative buoyancy factor when it is taken as the solute. The calculations imply that regardless of the concentration, the bromocamphor is expected to be more concentrated on the bottom and tristearin to be more concentrated on the top. This brings to mind a metaphysical necessity for all two component solutions: if one component is more concentrated on the top, the other must be more concentrated at the bottom.

The tristearin - bromocamphor system is useful for another purpose. The density data are available for three different temperatures. In table II, this data has been used to show that the concentration ratio is a function of temperature as would be expected from the fact that the buoyancy factor varies with temperature.

KINETIC EQUATIONS AND CALCULATIONS

Although we have seen that at equilibrium, a gravitational field can produce a detectable concentration gradients in a variety of systems, one must be sure that equilibrium of this sort can be approached in a reasonable time frame.

The equilibrium which we are discussing is brought about by diffusion. However, normal diffusion equations predict a uniform equilibrium concentration. It becomes obvious that for our application, the diffusion equations must be derived incorporating the effect of a gravitational field. To treat the effect of a gravitational or other type of field, one needs to consider only one dimensional diffusion. When a gravitational field is not considered, the following one dimensional equations are applicable (ref. 13).

$$F_1 = - D_1 \frac{dC_1}{dX} \quad (20)$$

and

$$\frac{dC_1}{dt} = - \frac{dF_1}{dX} \quad (21)$$

where F_1 is the flow ($\text{g}/\text{cm}^2/\text{sec}$); D , the diffusion coefficient (cm^2/sec); C_1 , the concentration (g/cm^3); X , the distance (cm); and t , the time (sec). Diffusion proceeds parallel to the concentration gradient. To include the effect of gravity on diffusion, one must return to the derivation of the diffusion equations.

Jump Frequency Approach

One of the derivations for the diffusion equations starts with the concept of a molecule jumping from one position to another in a material. Reference

to figure 2 will aid in the visualization. One may set up the following equation for a solution that obeys Henry's law.

$$F_1 = - \alpha_1 \left\{ C_1'' \exp \left(\frac{E_1' - Q_1}{kT} \right) - C_1' \exp \left(\frac{(E_1' - Q_1)}{kT} \right) \right\} / (X'' - X') \quad (22)$$

where F_1 is the flow; α_1 , the proportionality constant; X' , the distance parameter of the starting position (being farther away from the gravitational source); X'' , the distance parameter of the position after the jump (being closer to the gravitational source); C_1' , the concentration of species 1 at X' ; C_1'' , the concentration at X'' ; k , the Boltzman constant; E_1' , the extra energy of the system due to the presence of an i 'th molecule, before the jump; E_1'' , the corresponding value after the jump; and Q_1 , the extra energy of the system due to the presence of the i 'th molecule in the activated position for diffusion (essentially halfway between the initial and final positions).

As X'' approaches X' , equation (22) becomes:

$$F_1 = - V_1 \left\{ \frac{dC_1'}{dX} + \left(\frac{C_1'}{kT} \right) \frac{dE_1'}{dX} \right\} \exp \left(\frac{-Q_1 + E_1'}{kT} \right) \quad (23)$$

the C_1' may be written simply as C_1 ; the $\alpha_1 \exp\{(-Q_1 + E_1')/kT\}$ may be replaced by D_1 , the diffusion coefficient; and E_1'/RT may be substituted for E_1'/kT where E_1' is the extra energy of the system due to the presence of a mole of species 1. Thus,

$$F_1 = - D_1 \left\{ \frac{dC_1}{dX} + \left(\frac{C_1}{RT} \right) \frac{dE_1}{dX} \right\} \quad (24)$$

The first term in equation (24) corresponds to the relation expressed in equation (20). The second term in equation (24) corresponds to the change in potential energy of the system due to a molecule's position in a gravity field as the molecule moves toward the gravitational source. Thus far, equation (24) is applicable to any type of field because we have not yet introduced the actual dependence of the energy upon position in a gravitational field. Note that equation (24) has the same form as that for an ion in an electrical field (ref. 9, eq. (5) in Chap. 6).

The change of the concentration with time is dependent solely on the flow gradient as described in equation (21). It is independent of any field which might exist. Combining equations (21) and (24) yields:

$$\frac{dC_1}{dt} = D_1 \left\{ \frac{d^2 C_1}{dX^2} + \frac{\left(\frac{dE_1}{dX} \right) \left(\frac{dC_1}{dX} \right)}{RT} + \left(\frac{C_1}{RT} \right) \frac{d^2 E_1}{dX^2} \right\} \quad (25)$$

Energy Versus Height

Equation (26) relates the change of E_1 with X within a gravity field.

$$\frac{dE_1}{dX} = - gB_1 \quad (26)$$

where g and B_i are assumed not to be a function of X so that $d^2E_i/dX^2 = 0$. In equation (26) as in earlier equations, the expression $\bar{V}_{i\rho}$ is the weight of solution corresponding to the volume of one mole of the i 'th species. Substituting equation (26) into equations (24) and (25) yields, respectively:

$$F_i = - D_i \left(\frac{dC_i}{dX} - \frac{C_i g B_i}{RT} \right) \quad (27)$$

$$\frac{dC_i}{dt} = D_i \left\{ \frac{d^2 C_i}{dX^2} - \left(\frac{g B_i}{RT} \right) \frac{dC_i}{dX} \right\} \quad (28)$$

Equilibrium

At equilibrium, F_i in equation (27) becomes zero. The resultant equation may be integrated if the solution is dilute and noncompressible.

$$RT \ln \left(\frac{C_i''}{C_i'} \right) = g B_i \quad (29)$$

The C_i''/C_i' may be replaced by N_i''/N_i' , and equation (29) becomes equation (10). It should be noted that for the derivation of equation (29), the solution did not have to obey Raoult's law; only Henry's law has to be obeyed.

Alternate Derivation

Equations (27) and (28) can be derived in a simpler and less rigorous fashion. In this alternate derivation, one can determine more easily the expression to be used for B_i if the diffusing species is an ion. The derivation involves subtracting the equilibrium value of dC/dX from its actual value in equation (20). Thus,

$$F_i = - D_i \left\{ \frac{dC_i}{dX} - \left(\frac{dC_i}{dX} \right)_e \right\} \quad (30)$$

where the subscript e refers to the equilibrium condition. For a dilute solution, equation (14) can be written as follows:

$$\left(\frac{dC_i}{dX} \right)_e = C_i g \frac{(M_s - \bar{V}_s \rho)}{Y} \quad (31)$$

where the $Y = 1$ for an uncharged diffusing species. Combining equation (30) and (31) result in the diffusion equation for an ion.

$$F_i = D_i \left\{ \frac{dC_i}{dX} - C_i g \frac{(M_s - \bar{V}_s \rho)}{YRT} \right\} \quad (32)$$

Equation (32) is just a more detailed way of writing equation (27). Thus, equations (27) and (28) apply to ionic diffusion where $B_1 = (M_s - \bar{V}_s \rho) / Y$.

Program

Equation (28) is not readily integrated. But with modern computers, integration is not required to make equation (28) useful. A simple Basic computer program implementing equation (28) is given in table III; it yields the concentration and concentration gradient profiles as a function of time. The program is written for an initially uniform concentration and with the following set of default parameters: buoyancy factor equal 100 g/mol; 100 000 G's; $D = 1 \times 10^{-5}$ cm²/sec; $h = 1$ cm; and 20 finite elements.

Kinetic Plots

Our calculations via the program in table III are shown graphically in figures 3 to 8. The solid lines in figure 3 gives the concentration profile for various periods of time, using the default parameters. These default parameters represent a typical solute - liquid solvent system under ultracentrifuge conditions. The points represent calculations using 100 finite elements; these are in good agreement with its respective line for which only 20 finite elements were used. Note in figure 3 that initially only the concentrations at the top and bottom of the column change. This is in accord with equation (28): initially, there are no concentration gradients present except for the discontinuities at the top and the bottom. Thus initially according to equation (28), only the concentrations at the top and bottom should change. As time proceeds, the concentration gradients move toward the middle of the column accompanied by changes in the concentrations.

One can also see in figure 3, that equilibrium is approached in about 50 000 sec (about 13 hr). This is a reasonable time frame for an ultracentrifuge experiment intended to measure such a concentration gradient. Figure 4 is a similarly calculated profile for the concentration of sodium chloride in the ocean, using its buoyancy factor from table I and a diffusion coefficient of 1.54×10^{-5} cm²/sec (ref. 14). For this system, equilibrium is approached in about 10^{16} sec (about 500 million years). Because of this long time period and the almost constant motion of the ocean, it is doubtful that gravitation equilibrium of sodium chloride in the ocean will ever be approached.

Figure 5 shows a "concentration" profile that allows a fuller comprehension of the approach to equilibrium. In figure 5 the ratio of the concentration change to the concentration change at equilibrium is plotted as a function of the distance from the bottom of the column. Thus, the ordinate represents the fraction of the equilibrium achieved for the time period indicated for a particular curve. The default parameters were used. A similar type profile for the concentration gradient is given in figure 6. Both figures 5 and 6 show that equilibrium is very closely approached after 50 000 sec. Figure 6 shows that the concentration gradients at the top and bottom are achieved immediately. But this does not mean that the concentration itself reaches equilibrium; see figure 5.

The irregularities near the middle of the curves in figure 5 are a result of the fact that the position at which the equilibrium concentration equals

the initial concentration moves with time. This in turn results from the fact that the ends of the equilibrium profile are not perfectly symmetric with respect to the middle position of the column as can be seen in figure 5. However, when the gravitational equilibrium effect (product of g and the buoyancy factor) is small, the profile is more symmetric, and the irregularities disappear. This is illustrated by the points in figure 5 which represent $G = 1$ and a buoyancy factor of 100. However, the essential features in figure 5 are independent of G and the buoyancy factor; thus, the fraction of equilibrium achieved is essentially independent of these two parameters: g and B_1 .

In any experimental investigation, measurement of only the upper and lower concentrations is all that would be necessary to establish the "equilibrium" values for the gravitational effect. Therefore, one can use the fraction of equilibrium achieved at the top and bottom of a column as an overall measure of the fraction of equilibrium achieved. To obtain a single value for the top and bottom, the product of G and the buoyancy factor can be assumed to be small. With these two assumptions, figure 7 is plotted: the fraction of total change of concentration at the top (and bottom) is the abscissa, and the log of time is the ordinate. The dotted line represents the default values of the diffusion coefficient (10^{-5} cm²/sec) and height (1 cm). The time required to achieve over 96 percent equilibrium is not graphed in figure 7 because it has nearly a vertical slope. Remember that equilibrium is never achieved in a finite time frame.

Effect of D and h

Via the computer program in table III, the concentration function profiles (similar to those in figure 5) can be calculated for various values of D and h . The values of the concentration function at the ends (top and bottom) are again plotted as a function of time in figure 7. Curves for a constant value of D/h^2 are superimposable. Undoubtedly, this fact could be proven mathematically starting with equation (28).

From figure 7, the time, t , required to achieve a certain degree of equilibrium is seen to be inversely proportional to the square of h . Because of this, the curves in figure 7 can be combined into the single curve in figure 8, where tD/h^2 is plotted as a function of the fraction of equilibrium (concentration change) achieved. Via this graph and the values of D and h , one can readily determine the fraction of equilibrium achieved. If one is content with 96 percent equilibrium, the following equation may be written as an approximation.

$$t = 0.3 \frac{h^2}{D} \quad (33)$$

where 0.3 is a unitless value. For our default values, the time predicted by equation (33) is 30 000 sec (about 9 hr). In contrast for sodium chloride in the ocean, the time required for 96 percent equilibrium is predicted to be about 2×10^{16} sec (roughly a billion years). Because the time to approach equilibrium is dependent only on D and h , and the D for all ions are quite similar, roughly the same time to approach equilibrium in the ocean is required by all salts.

Solid Solutions

The default parameters for the computer program in table III represent a solute in a liquid solution because the diffusion coefficient used is 10^{-5} cm^2/sec . The diffusion coefficient of the solute in a solid solution can be several orders of magnitude lower. Equation (33) would predict t to be 900 hr when the diffusion coefficient of the solute is 10^{-7} cm^2/sec . This time is likely too long for an ultracentrifuge experiment.

Gases

Gases exhibit diffusion coefficients in the range of 10^{-4} cm^2/sec , larger than those for solutes in liquid solutions. Thus according to equation (33), a 1 cm high column of gas would approach equilibrium in less than an hour. For a gas, the buoyancy factor is its molecular weight which is in general larger than the buoyancy factor for a solute in a solution ($M_1 - V_1\rho$). Thus, the gravitation - concentration effect should be more easily observable in a gas than in a liquid solution with the assumption that both are under the same gravitational conditions, e.g., 100 000 G with $h = 1$ cm. Under a lower gravitational force, h would have to be larger to observe the same difference in concentration between the top and bottom of the column. This would require a longer equilibrium time. If one sets the maximum time at 10 hr then equation (33) gives a height of about 4 cm for the column of a gas.

Summary of the Kinetics

Figure 8 and equation (33) summarize our findings concerning the kinetics of gravitational induced concentration gradients. The fraction of gravitational equilibrium achieved is directly proportional to the diffusion coefficient and inversely proportional to the square of the height of the column. The time required to attain essentially 96 percent equilibrium is given by equation (33). This equation shows that the diffusion induced by gravity is a very slow process; in general, very long times are required to approach equilibrium. Only for low values of h , about 1 cm or less, is equilibrium approached in a reasonable time period, less than 10 hr. Gravitational - concentration equilibrium in the ocean would require a billion years. Gravitational equilibrium is therefore not approachable because the convection in the ocean operates on a smaller time scale.

Even if the kinetics are favorable, the equilibrium values themselves must be sufficiently different from the original concentration; see equation (10). This means that the gravitation constant must be large, of the magnitude achievable in an ultracentrifuge.

Although attainment of concentration equilibrium is a slow process, figure 5 indicates that concentration equilibrium at the top and bottom of any column is achieved immediately. Unfortunately, this is a very small gradient under normal gravity conditions: 0.001 percent/cm for sodium chloride in the ocean (or any column of water at 1 G). However, if a device were built that could measure such a small gradient, detection of the gravitational - concentration effect would cease to be a kinetics problem.

SPECIAL TOPICS

Ionic Species

As we have seen earlier, equation (14) describes the variation of the concentration of an ionized salt in a solution subject to a gravitational field. However, equation (14) is valid only when a single salt is present in solution. One way to obtain a more general equation is to start with the following equation.

$$\sum \left(b_i \frac{dC_i}{dh} \right) = 0 \quad (34)$$

where b_i is the valence of an ion (it is negative for an anion); and the summation is over all the cations and anions present. The equation merely states that an electrical charge gradient cannot exist, even in a gravitational field. Also required is an equation that relates concentration gradients to buoyancy factors.

$$\frac{\frac{dC_i}{dh}}{b_i C_i} - \frac{\frac{dC_j}{dh}}{b_j C_j} = \frac{g \left(\frac{B_i}{b_i} - \frac{B_j}{b_j} \right)}{RT} \quad (35)$$

This equation can be derived in the same manner as equation (7) by combining the equations for two different ions so that the effect of electrical charge is eliminated from the calculation. In equation (35) both subscripts, i and j , refer to any ion present; note that the b 's are negative for anions. By combining equation (34) and (35) followed by simplification, one obtains:

$$RT \frac{d \ln(C_i)}{dh} = g b_i \frac{\sum (B_{i,j} C_j b_j^2)}{\sum (C_j b_j^2)} \quad (36)$$

or

$$RT \ln \left(\frac{C_i''}{C_i'} \right) = g h b_i \frac{\sum (B_{i,j} C_j b_j^2)}{\sum (C_j b_j^2)}$$

where the summations are again over all the ions present; and $B_{i,j} = B_i - B_j = B_s (1/b_i - 1/b_j)$. When i and j are both anions or both cations, one may substitute $B_{i,k} - B_{j,k}$ for $B_{i,j}$ where the subscript k represents any cation when i and j are both anions, and k represents any anion when i and j are both cations. Thus, the use of equation (36) does not require knowledge of the values of B for individual ions, only those for salts. The integrated form of equation (36) is only an approximation because all the concentrations, C_j , are functions of h . However, equation (36) allows one to demonstrate the general dependence of concentration ratios on the composition of a solution.

Our first example is an aqueous solution of sodium chloride and ferric chloride. Figure 9 is a plot of the concentration ratio of each ion as a function of the relative concentration of the two salts: the cation fraction of the ferric ion. The conditions assumed are 100 000 G's and $h = 1$ cm. The actual concentrations of the salts need not be specified. However, the plot in figure 9 is more precise for very dilute solutions. The data used in the plot are available in table I. Note that the ratio N''/N' for both cations varies with composition even though each of these cations can exist only as the chloride. Only when one salt predominate in a solution will equation (14) yield a precise ratio of N''/N' for that salt. This is illustrated in figure 9 by the fact that the N''/N' of both the sodium and chloride ions approach the value for sodium chloride (table I) near zero ferric ion concentration.

A more complex example involves the mixture of two salts without a common ion. This means that two cation and two anions are present, and thus the solution really contains four salts. The desired calculations can only be made when the buoyancy values of all four salts are known. The example to be used is a solution of sodium chloride and potassium nitrate, which includes following ions: Na^+ , K^+ , Cl^- and NO_3^- . The results of the calculations are plotted in figure 10. The same parameters are used as are used for figure 9: 100 000 G's and $h = 1$ cm. Again one finds that the N''/N' ratio for each of the ions varies with the concentration parameter.

To plot the values of N''/N' as a function of all the ions present in two salts (without a common ion) would require at least a pseudo-three dimensional graph. Treatment of solutions with more than two salts would require multidimensional graphs. Thus, application of equation (36) to multisalt systems is best accomplished by restricting calculations to the composition(s) of particular interest.

Osmosis

Generally the van't Hoff equation (ref. 15) is used to express osmotic pressure: $P_{os} = N_2RT/V_1$ where 2 refers to the solute; and 1 to the solvent. Let us envision a vertical semipermeable membrane separating a solution containing a solute from the pure solvent. A pressure equal to the osmotic pressure is applied to the solution side so that the surfaces of both the pure solvent and the solution will be at the same level. Under these conditions, there will be a hydrostatic pressure difference, ΔP_{hy} , between the two sides of the membrane which increases with depth according to the following equation.

$$\frac{d \Delta P_{hy}}{dh} = g(\rho - \rho_j) \quad (37)$$

where j refers to the pure solvent. For equilibrium to exist at all depths, the osmotic pressure would have to vary in the same way with h . To substantiate this, one can start with a different formulation of the osmotic pressure equation (ref. 15).

$$P_{os} = - RT \frac{(\ln N_1)}{V_1} = - RT \frac{(\ln N_j)}{V_j} \quad (38)$$

where the final form of the equation uses our subscript notation. If V_j is assumed to be independent of h , differentiation of equation (38) yields:

$$\frac{dP_{os}}{dh} = \frac{-RT}{V_j} \frac{d \ln(N_j)}{dh} \quad (39)$$

Substituting the value of $d \ln(N_j)/dh$ from equation (9) into equation (39) yields:

$$\frac{dP_{os}}{dh} = \frac{g(M_j - V_j \rho)}{V_j} = g(\rho - \rho_j) \quad (40)$$

The final form of the equation results from the fact that $\rho_j = M_j/V_j$. Comparison of equations (37) and (40) shows the correspondence between the change in osmotic pressure with h and the change in hydrostatic pressure with h .

Vapor Pressure

Let us now apply equation (10) to the concept of vapor pressure. Assume that we have a pure liquid with a vapor that behaves ideally. A liquid with a low vapor pressure will suffice. Actually, one could consider a solid just as well as a liquid. For such a material the fugacities in equation (15) can be replaced by the vapor pressures because the fugacity is the idealized vapor pressure.

$$RT \ln \left(\frac{P''}{P'} \right) = P(\text{applied})V \quad (41)$$

where V is the volume of a mole in the condensed state. Equation (41) states that the vapor pressure of a material increases with an increase in the applied pressure. However, generally the effect is quite small. The effect of the earth's atmosphere on the vapor pressure of water at 20 °C is only about 0.07 percent.

In equation (41) the applied pressure may be the hydrostatic pressure of the liquid itself which changes with depth; $P = \rho gh$. Interpretation of equation (41) in this manner tells us that the vapor pressure at the bottom of an isothermal liquid in a gravitational field is somewhat greater than that at the top.

Equation (15) can be modified still further; the applied pressure can be assumed to be the vapor pressure. Thus, we have

$$RT \ln \left(\frac{P''}{P'} \right) = P''V \quad (42)$$

In this equation, P' is the vapor pressure measured under vacuum (Langmuir) conditions while P'' is the value obtained under equilibrium (Knudsen) conditions. Equation (42) shows us that from a theoretical viewpoint the two are not identical. However, from a practical viewpoint, the difference is negligible. For water which has a vapor pressure of about 17.5 mm of Hg at 20 °C, the Knudsen pressure would be only 0.0017 percent greater than the Langmuir value.

For ethanol which has a vapor pressure of about 42 mm of Hg at 20 degrees, the Knudsen pressure would be 0.008 percent greater than the Langmuir pressure.

We have applied equations (41) and (42) to only pure materials. However, they may be applied just as validly to components in an ideal solution.

Two Continuous Phases In Contact

If two phases are set up as side-by-side columns, and each phase is assumed to be in equilibrium with respect to h , equation (18) holds for all the components of both phases. As a result

$$\frac{f_{1,1}''}{f_{1,1}'} = \frac{f_{1,2}''}{f_{1,2}'} \quad (43)$$

where the 1 and the 2 refer to the two different phases. The system is most easily visualized in terms of a solid and a gas, but the concept is valid for solid - solid, solid - liquid, liquid - liquid, and liquid - gas systems. Systems involving two fluids requires the visualization of semipermeable membrane between the phases.

Let equilibrium be assumed to exist between the two phases at the higher altitude. In other words, $f_{1,1}' = f_{1,2}'$ for each component. As a consequence of equation (43), $f_{1,1}'' = f_{1,2}''$ for each component. Thus, if two phases are in equilibrium with respect to h , and in equilibrium with each other at one altitude, they are in equilibrium at all altitudes. Under these conditions no net transport of any species is expected. Let us restate the conclusion for a more specific case. A column of a single phase solid setting in an atmosphere of its own vapor is not expected to be transported from a higher elevation to a lower elevation. This also means that extraction coefficients based on fugacities do not vary with position in a gravitational field; this does not mean that an extraction coefficient based on concentrations will not vary with h .

Two Phases In Contact, One Not Continuous

Phase 2 is now assumed to be noncontinuous while phase 1 is still continuous. One portion of the noncontinuous phase 2 is allowed to contact the column of phase 1 at one altitude, and another portion of phase 2 is allowed to contact the column of phase 1 at another altitude, a distance h below the first. In this case, equation (18) applies to the components in the continuous phase but not to those in phase 2. For phase 2 the fugacity of a component is determined by the pressure exerted by the continuous phase 1.

$$RT \ln \left(\frac{f_{1,2}''}{f_{1,2}'} \right) = \bar{V}_{1,2} P = \bar{V}_{1,2} \rho_1 gh \quad (44)$$

where $\bar{V}_{1,2}$ is the partial molal volume of species 1 in phase 2, and the pressure at the higher elevation is assumed to be nil.

Next let us assume that equilibrium exists at the higher altitude.

$$f_{i,2}^i = f_{i,1}^i \quad (45)$$

Combining equation (18) for phase 1 with equations (44) and (45) yields

$$RT \ln \left(\frac{f_{i,1}^i}{f_{i,2}^i} \right) = (M_i - \bar{V}_{i,1} \rho_1) gh \quad (46)$$

thus, the fugacities of species i are not the same in both phases at depth h . Transport of species i between the phases is expected. If the buoyancy factor is positive, transport at depth, h , will be from phase 1 to phase 2 because the fugacity is greater in phase 1. This will cause a displacement of phase 1 from gravitational equilibrium; and eventually at the higher elevation, species i will tend to be transported from phase 2 to phase 1. Recall that such transport is not predicted when both phases are continuous. The transport in the case of a noncontinuous phase is due to the fact that the lower portion of the noncontinuous phase is not subjected to a hydrostatic pressure equal to that of a column of phase 2, h in height.

Under the conditions where transport does occur between different elevations, the mechanism varies depending upon whether the phase 1 is condensed or a gas. When phase 1 is a gas, transport occurs by vaporization - condensation, and the rate of transport depends upon the vapor pressure of the species in phase 2 (or the vapor pressure of phase 2 itself if it is a pure material). Thus for very low vapor pressures, the transport could be undetectable. When phase 1 is a liquid or solid, transport would occur by solution - diffusion - dissolution. The rate of transport will be highly dependent on the solubility of phase 2 in phase 1. Low solubility would mean that transport would essentially be nil.

Transport can occur even if none of the material to be transported is at the lower elevation; only nucleation sites are required. Consider the following example. A container is filled with an aqueous saturated salt solution and a crystal of the salt is adhering to the side and near the top of the container. Equation (46) predicts that the crystal of salt will tend to dissolve and recrystallize near the bottom of the container. (Evaporation of the water is assumed to be nil.)

When phase 2 is a metal, transport can occur electrochemically if certain conditions are met. The metal at the upper position must be connected electrically to the metal in the lower position. The column of liquid must contain an electrolyte. Finally, the electrochemical transition between the metal and its ion must be reversible. Without the short circuit between the two identical pieces of the metal (each at a different elevation), a small voltage would exist between them. Such a voltage would not only be dependent upon the chemical potential difference between the two electrode but upon the transference numbers of the ions involved. Thus, a discussion of the voltage generated becomes too far outside the scope of this report.

Multiphase Systems

From the preceding sections, one can see that a multiphase system can be in equilibrium only when all the phases are continuous. If one phase is non-continuous, complete equilibrium between various parts of such a phase is not possible. This follows from equation (46). If diffusion between phases is permitted, the system would be unstable as the example of a salt in a saturated water solution. In contrast if diffusion between phases is not permitted, stability (but not equilibrium) of the system is possible. In such a multiphase system, equilibrium with respect to h for continuous phases can still exist; equations (10) and (18) would apply to the components in these phases. Equilibrium with respect to h for noncontinuous phases is not possible because $N_i'' = N_i'$ for all the components of such phases. The fugacities are determined by the hydrostatic pressure to which they are subjected; see equation (15). The hydrostatic pressure is given by ρgh , where the density, ρ , is that of a continuous phase surrounding the noncontinuous phase.

Solubility

Consider again, two columns of different phases in a gravitational field, each phase being in equilibrium with respect to h . Let phase 2 be of a pure condensed phase, and phase 1 be a saturated solution of phase 2 in some solvent. Equation (10) is applicable, and the N_i 's can be replaced by S_i 's, the solubilities.

$$RT \ln \left(\frac{S_{2,1}''}{S_{2,1}' } \right) = ghB_{2,1} \quad (47)$$

where $B_{2,1}$ is the buoyancy factor of phase 2 in phase 1; and $S_{2,1}$ is the solubility of phase 2 in phase 1.

Like equation (10) from which it was derived, equation (47) applies precisely only to dilute solutions. Therefore, equation (47) applies best to relatively "insoluble" materials. However, the partial molal volumes of such materials are sometimes difficult to measure. Therefore, the greatest application of equation (47) might be for more soluble materials where the equation would only be an approximation. For instance, equation (47) predicts about a 6 percent change (increase in the downward direction) in the solubility of sodium chloride in water for $h = 1$ cm and 100 000 G's. The values of $V_{2,1}$ and ρ used for the calculation are those in the vicinity of the saturation concentration.

The ratio of solubilities of a noncontinuous phase 2 in a continuous phase 1 may also be expressed as a function of h . The fugacity ratio for phase 2 is determined by the pressure exerted by phase 1. Thus,

$$RT \ln \left(\frac{f_2''}{f_2'} \right) = V_2 P = V_2 \rho gh \quad (48)$$

where V_2 is the molar volume of pure phase 2, and ρ is the density of the saturated solution (phase 1). Because saturation is assumed at both

altitudes, the fugacity of the dissolved phase 2 is equal to the fugacity of solid phase 2. Thus,

$$RT \ln \left(\frac{f''_{2,1}}{f'_{2,1}} \right) = V_2 \rho gh \quad (49)$$

Because Henry's law is assumed to hold, the ratio f/N for a nonionized material is constant for any particular value of h . This constant may be evaluated from the equilibrium values of f and N . Therefore, the dependence of f/N on h is the same as for the dependence of their equilibrium values on h , which can be ascertained by combining equations (10) and (18).

$$RT \ln \left\{ \frac{\left(\frac{f''_{2,1}}{N''_{2,1}} \right)}{\left(\frac{f'_{2,1}}{N'_{2,1}} \right)} \right\} = \bar{V}_{2,1} \rho gh \quad (50)$$

where the $\bar{V}_{2,1}$ is the partial molal volume of phase 2 in phase 1, not the molar volume of pure phase 2. By combining equations (49) and (50) and substituting S 's for N 's because the concentrations correspond to solubilities, one obtains:

$$RT \ln \left(\frac{S''_{2,1}}{S'_{2,1}} \right) = gh \rho (V_2 - \bar{V}_{2,1}) \quad (51)$$

The same equation may be derived for ionized salts. Moreover, it may be derived in a manner which shows it is not limited to dilute solutions. To apply equation (51) we again use a 1 cm high column of an aqueous solution of sodium chloride at 100 000 G's. The change in solubility predicted is less than 2 percent, less than the change in solubility (6 percent) predicted when sodium chloride is a continuous phase.

The ρgh in equation (51) may be replaced by P , the hydrostatic pressure.

$$RT \ln \left(\frac{S''_{2,1}}{S'_{2,1}} \right) = (V_2 - \bar{V}_{2,1}) P \quad (52)$$

From this equation one sees that the solubility change with h for a non-continuous phase can be attributed solely to the hydrostatic pressure of the solution.

Equilibrium Constants

The fact that solubility changes with h , leads to the question whether other types of equilibrium constants change with h . An equilibrium constant at the higher position in a gravitational field is defined as follows.

$$K' = \frac{\prod (f_j^{y_j})}{\prod (f_i^{y_i})} \quad (53)$$

where i refers to the reactant species; j , to the product species; and the y 's, to the coefficients of the species in the chemical reaction under consideration. By restricting the equilibrium constant to molecular (nonionic) reactions, equation (18) for each molecular species may be substituted into equation (53).

$$K' = \left\{ \frac{\prod (f_j''^{y_j})}{\prod (f_i''^{y_i})} \right\} \exp \left[\{ \sum (y_i M_i) - \sum (y_j M_j) \} \frac{gh}{RT} \right] \quad (54)$$

But $\sum (y_i M_i) = \sum (y_j M_j)$ so that

$$K' = \frac{\prod (f_j''^{y_j})}{\prod (f_i''^{y_i})} \quad (55)$$

The right side of equation (55) is the definition of the equilibrium constant at the lower positions, K'' ; this shows that equilibrium constants involving molecular species and based on fugacities are independent of depth in a gravity field.

Polymers

Let us write equation (10) for an addition polymer, assuming that $\bar{V}_p = p' \bar{V}_i$ where i represents the monomer; p , the polymer; and p' , the number of monomer units in the polymer.

$$RT \ln \left(\frac{N_p''}{N_i^{p'}} \right) = p' (M_i - \bar{V}_i \rho) gh \quad (56)$$

Combining this equation with equation (12) for the monomer gives the following relationship.

$$\frac{N_i^{p'}}{N_p'} = \frac{N_i''^{p'}}{N_p''} \quad (57)$$

Thus at gravitational equilibrium, the value of $N_p/N_i^{p'}$ is a constant independent of h , even though the polymer concentration may not be in equilibrium with the monomer concentration. Combining equation (57) with equation (12),

$$\frac{N''_D}{N'_1} = \left(\frac{N''_D}{N'_1} \right) \exp\{(p' - 1)gh(M_1 - \bar{V}_1\rho)\} \quad (58)$$

Because M_1 is expected to be greater than $\bar{V}_1\rho$, the ratio of N''_D/N'_1 should increase with depth if equilibrium with respect to h exists.

When equilibrium also exists between the polymer and the monomer concentrations, equation (56) states that the equilibrium constant (based on concentrations) is independent of h , providing $\bar{V}_D = p'\bar{V}_1$. In a similar manner it can be shown that the equilibrium constant (in terms of concentrations) for any reaction is independent of h if the sum of the molal volumes of the products is equal to the sum of the molal volumes of the reactants.

Near the Critical Solution State

The variation in concentration in a gravitational field seems to be most easily observed near a critical solution temperature. Most if not all investigations of this phenomenon have involved two component systems. At the critical temperature and critical composition, such a system separates into two phases. In the single phase region near the critical point, one might expect that molecules of like species would cluster together to form what might be called physical polymers (molecules held together by physical not chemical forces). Acceptance of this concept of physical polymers near the critical point would mean that equation (56) could apply. Via experimental data, equation (56) could be used to calculate a value for p' ; p' would be an estimate of the number of molecules in a cluster (or polymer) of the component.

Extrapolation to Higher Concentration

To apply equation (7) to solutes of higher concentration, one must express the density in terms of the mole fraction of species i . In this treatment the solution will be considered to contain only one solute.

$$\rho = \frac{M_j + N_1(M_1 - M_j)}{\bar{V}_j + N_1(\bar{V}_1 - \bar{V}_j)} \quad (59)$$

Substitution of this equation into equation (7) and expansion of reciprocals to only the first power of N_1 results in the following:

$$\left[\frac{1}{N_1} + \frac{\left(\frac{\bar{V}_1}{\bar{V}_j}\right) - \left(\frac{M_1}{M_j}\right)}{\left(\frac{M_1}{\bar{V}_1\rho_j}\right) - 1} \right] dN_1 = (M_1 - \bar{V}_1\rho_j)g \frac{dh}{RT} \quad (60)$$

where i refers to the solute; j , to the solvent; and ρ_j is the density of the solvent. To integrate equation (60) one must still assume a constant \bar{V}_j and noncompressibility of the solution.

$$RT \ln\left(\frac{N_j''}{N_j'}\right) + RT(N_j'' - N_j') \frac{\left(\frac{\bar{V}_j}{\bar{V}_j}\right) - \left(\frac{M_i}{M_j}\right)}{\left(\frac{M_i}{\bar{V}_j \rho_j}\right) - 1} = (M_i - \bar{V}_j \rho_j)gh = RT \ln\left(\frac{N_j''}{N_j'}\right)_x \quad (61)$$

where the subscript x refers to the value of N_j''/N_j' calculated from equation (10). Equation (12) is then used to calculate N_j' . Finally, equation (61) can be used to obtain a closer approximation for the ratio N_j''/N_j' .

Suspensions

Let us now return to Perrin's work (ref. 5) involving a suspension of particles in a liquid. The fact that equation (5) is obeyed leads to an interesting inference. Note that equation (5) treats each suspended particle as a molecule, and that equation (5) specifies a mole of suspended particles. This is clear from the occurrence of Avogadro's number in the equation. If one attributes a molecular weight, M_s , and a molecular volume, V_s , to the particles, equation (5) becomes

$$RT \ln\left(\frac{n_0}{n}\right) = (M_s - V_s \rho)gh \quad (62)$$

Because equation (62) has the same form as equation (10), and equation (10) can be viewed as a balance of chemical and gravitational potentials, one can postulate that a similar balance gives rise to equations (5) and (62). Thus, a chemical potential could be attributed to suspended particles in a fluid, just as one is attributed to a solute in a solvent. However, remember that for the suspension, an Avogadro's number of particles is taken as a mole of the material.

Suggested Microgravity Experiment

Equation (52) tells us that via pressure one can increase the solubility of a solute. Releasing the pressure would cause crystals of the solute to form. The purity, size, and perfection of these crystals would depend on the slowness at which the pressure is released. In 1 G, a difference in density between the crystals and the solution can induce convection that can limit the perfection of the crystals. However, under microgravity conditions, the convection would be minimal, and the resultant crystals should be more perfect.

An example would be the recrystallization of sodium chloride from water. The difference between the molar volume of the solid and its molal volume in solution is about 9.3 cc. With an applied pressure of 100 atm, an increase in solubility of about 4 percent is expected. For a liter of solution and a

solubility of 0.357 g/cc under zero applied pressure, the expected yield is 14 g. This is more than required to test the method.

SUMMARY OF FINDINGS

Under equilibrium conditions, the fugacity of molecular and ionic species is a function of the position in a gravitational field: equation (18). This effect is partly due to the hydrostatic pressure of the material above it: equation (15). The rest of the effect is associated with a concentration gradient necessary for equilibrium: equation (10). For multiple ionic species, equation (36) can be applied. The concentration effect is generally less than 0.1 percent for a meter column at 1 G. But under ultracentrifuge conditions of 100 000 G's, over a 10 percent difference is generally expected between the concentration at the top of a 1 cm column as compared with its concentration at the bottom, tables I and II. The ocean's depth could lead to even greater concentration gradients for the salts present. However, the existence of fluid convection inhibits the attainment of such equilibrium.

Modifications of the usual diffusion equations are necessary to treat the achievement of concentration equilibrium in a gravitational field: equations (27) and (28). The important parameters for approaching equilibrium are the diffusion coefficient and the height of the column. Figures 7 and 8 give the time required to achieve various fractions of equilibrium. Equation (33) gives the time required to achieve 96 percent equilibrium. For 96 percent equilibrium in a 1 cm high column, about 9 hr are required for a liquid solution. As the height increases, the time required becomes extremely long; gravitational equilibrium in the ocean requires about a billion years.

Under certain conditions a gravity field can give rise to bulk mass transport: equation (46). Another effect of a gravitational field is the existence of solubility gradients: equations (47) and (51). However, equilibrium constants and extraction coefficients based on fugacity are not affected by a gravity field. Moreover, the dependence of fugacity on depth and pressure helps explain some details of osmotic pressure and vapor pressure.

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TABLE I. - PARTIAL MOLAL VOLUMES AND CONCENTRATION RATIOS OF SOLUTES IN AQUEOUS SOLUTION IN A GRAVITATIONAL FIELD
(Temperature = 20 °C)

Solute	Species per molecule	Mole weight	Part. molal vol.	Buoyancy factor	Conc. ratio (a)	Conc. ratio (b)	Conc. ratio (c)	Conc. range percent	Conc. ratio (d)	Fuga. ratio (e)
Acetic acid	1	60.05	51.05	8.955	1.000	1.036	1.433	30	1.028	1.273
Acetone	1	58.05	66.18	-8.10	.9999	.9678	.7215	9.5	.9706	1.263
Ammonium chloride	2	53.5	36.40	8.531	1	1.034	1.409	.5	1.033	1.240
Ammonium hydroxide	1	35.05	42.42	-7.33	.9999	.9709	.7444	58	.9799	1.151
Ammonium sulfate	3	132.1	53.09	26.32	1	1.111	2.885	.5	1.109	1.702
Barium chloride	3	208.2	25.79	60.80	1	1.277	11.55	.5	1.275	2.312
Calcium chloride	3	110.9	20.34	30.19	1	1.129	3.371	.5	1.130	1.563
Cesium chloride	2	168.3	41.37	63.41	1	1.290	12.84	2	1.290	1.969
Citric acid	1	192.1	115.4	76.57	1	1.361	21.80	1	1.364	2.166
Cobalt chloride	3	129.8	13.50	38.77	1	1.168	4.761	.5	1.168	1.686
Copper sulfate	2	159.6	-2.36	80.99	1	1.385	26.04	.5	1.387	1.901
Creatinine	1	113.1	86	27.06	1	1.115	2.972	.5	1.119	1.576
Dextran	1	72 000	43 257	28 699	1.122	(f)	(f)	5.5	(f)	(f)
Ethanol	1	46.07	55.30	-9.17	.9999	.9637	.6911	9	.9713	1.203
Ethylene glycol	1	62.07	54.62	7.427	1	1.030	1.348	9.5	1.029	1.283
Ferric chloride	4	162.2	23.30	34.71	1	1.149	4.044	.5	1.149	1.921
Formic acid	1	46.03	33.63	12.34	1	1.050	1.643	7	1.047	1.203
Fructose	1	180.1	110.1	69.77	1	1.324	16.58	52	1.259	2.064
Glucose	1	180.1	111.8	68.22	1	1.316	15.58	4.5	1.310	2.064
Glycerine	1	92.09	70.04	21.96	1	1.092	2.420	58	1.069	1.448
Hydrochloric acid	2	36.47	18.28	9.083	1	1.037	1.441	1.5	1.036	1.158
Inulin	1	5 200	3 227	1 969	1.007	2 767	(f)	5.5	2 344	(f)
Lactose	1	342.3	205.6	136.4	1	1.731	242.6	7.5	1.694	3.965
Lead nitrate	2	331.2	-2 460	1 423	1.005	307.2	(f)	.5	269.2	3.793
Lithium chloride	2	42.4	17.87	12.24	1	1.050	1.637	.5	1.051	1.186
Magnesium chloride	3	95.23	17.46	25.91	1	1.109	2.837	.5	1.109	1.467
Magnesium sulfate	2	120.3	-1.78	61.08	1	1.278	11.69	.5	1.277	1.623
Maltose	1	342.2	205.6	136.4	1	1.731	242.6	.5	1.752	3.965
Manganese sulfate	2	151	3.741	73.62	1	1.344	19.36	.5	1.342	1.836
Mannitol	1	182.1	116.7	65.35	1	1.300	13.88	.5	1.290	2.081
Methanol	1	32.04	37.81	-5.74	.9999	.9771	.7936	56	.9831	1.137
Nickel sulfate	2	154.7	-11.4	83.13	1	1.397	28.39	.5	1.390	1.864
Nitric acid	2	63.02	29.08	16.94	1	1.070	1.978	1.5	1.070	1.288
Phosphoric acid	1	98	43.27	54.66	1	1.246	9.027	.5	1.240	1.483
Potassium bromide	2	119	33.63	42.65	1	1.187	5.567	1	1.185	1.614

TABLE I. - Concluded.

Solute	Species per molecule	Mole weight	Part. molal vol.	Buoyancy factor	Conc. ratio (a)	Conc. ratio (b)	Conc. ratio (c)	Conc. range percent	Conc. ratio (d)	Fuga. ratio (e)
Potassium carbonate	3	138.2	14.37	41.26	1	1.180	5.263	.5	1.179	1.744
Potassium chloride	2	74.55	26.99	23.75	1	1.100	2.601	1.5	1.099	1.349
Potassium chromate	3	194.2	39.45	51.55	1	1.230	7.964	.5	1.229	2.185
Potassium dichromate	3	294.2	88.98	68.35	1	1.316	15.66	1	1.313	3.267
Potassium iodide	2	166	46.91	59.51	1	1.270	10.97	.5	1.273	1.950
Potassium nitrate	2	101.1	38.61	31.21	1	1.133	3.512	1	1.134	1.502
Potassium oxalate	3	166.2	46.96	39.71	1	1.173	4.946	1	1.173	1.952
Potassium dihydrogen phosphate	2	136	38.45	48.78	1	1.216	7.123	1	1.214	1.729
Potassium monohydrogen phosphate	3	174.1	25.02	49.69	1	1.221	7.391	.5	1.217	2.015
Potassium sulfate	3	174.2	35.40	46.26	1	1.204	6.436	.5	1.203	2.016
Propylene glycol	1	76.09	70	6.070	1	1.024	1.276	9.5	1.022	1.358
Silver nitrate	2	169.8	21.04	74.40	1	1.349	19.97	.5	1.342	1.981
Sodium acetate	2	82.04	39.48	21.24	1	1.089	2.352	.5	1.087	1.391
Sodium bicarbonate	2	84.02	23.74	30.11	1	1.128	3.360	1	1.127	1.402
Sodium bromide	2	102.9	22.95	39.95	1	1.174	4.993	.5	1.173	1.513
Sodium carbonate	3	106	-3.66	36.55	1	1.158	4.355	.5	1.157	1.532
Sodium chloride	2	58.45	17.67	20.37	1	1.085	2.270	.5	1.086	1.265
Sodium hydroxide	2	40.01	-4.55	22.28	1	1.093	2.452	.5	1.093	1.174
Sodium molybdate	3	205.9	29.58	58.76	1	1.266	10.64	.5	1.265	2.290
Sodium nitrate	2	85.01	27.39	28.78	1	1.122	3.185	.5	1.120	1.407
Sodium monohydrogen phosphate	3	141.9	.7063	47.09	1	1.208	6.654	.5	1.205	1.770
Sodium sulfate	3	142	14.77	42.41	1	1.186	5.513	.5	1.187	1.771
Sodium tartrate	3	194	58.69	45.09	1	1.198	6.140	1	1.199	2.183
Sodium thiosulfate	3	158.1	28.99	43.02	1	1.189	5.650	.5	1.190	1.889
Sodium tungstate	3	293.9	30.57	87.75	1	1.423	34.19	.5	1.426	3.264
Strontium chloride	3	158.5	19.63	46.28	1	1.204	6.443	.5	1.206	1.892
Sucrose	1	342.3	209.3	132.5	1	1.705	207.6	58	1.530	3.965
Sulfuric acid	2	98.08	31.83	33.06	1	1.142	3.784	1	1.139	1.484
Trichloroacetic acid	2	163.4	81.90	40.69	1	1.177	5.144	1	1.179	1.930
Urea	1	60.06	43.26	16.76	1	1.069	1.963	1	1.067	1.273
Zinc sulfate	2	161.4	-5.58	83.52	1	1.399	28.83	.5	1.397	1.915

^aDilute solution; 1 G; h = 1 m.

^bDilute solution; 100 000 G's; h = 1 cm.

^cDilute solution; 1 G; h = 10 000 m.

^dConc. indicated in 'range' column; 100 000 G's; h = 1 cm.

^e100 000 G's; h = 1 cm.

^fExceeds 10 to the 38th power.

TABLE II. - PARTIAL MOLAR VOLUMES AND CONCENTRATION RATIOS OF SOLUTES IN METALS AND ORGANIC SOLVENTS
IN A GRAVITATIONAL FIELD (Temperature = 20 °C unless otherwise specified)

Solute/solvent	Mole weight	Part. molal vol.	Buoyancy factor	Conc. ratio (a)	Conc. ratio (b)	Conc. ratio (c)	Conc. range percent	Conc. ratio (d)	Fuga. ratio (e)
Benzene	78.11	97.86	-122	0.9995	0.6105	0.0072	10	0.6595	1.369
/stannic chloride									
Bromocamphor	231.1	211.9	-83.4	.9996	.7130	.0339	11.12	.7250	2.551
/tristearin; 18 °C									
Ethanol/acetone	46.07	60.48	-1.91	.9999	.9923	.9258	5.455	.9957	1.203
Sodium nitrate	84.99	-1689	1241	1.004	136	(f)	.07	42.41	1.399
/methylamine; 25 °C									
Stannic chloride	260.5	161.2	115.6	1	1.592	105.1	10	1.664	2.853
/benzene									
Tristearin	891.4	511.2	365.3	1.001	4.395	(f)	20	3.883	37.06
/bromocamphor; 18 °C									
Tristearin	891.4	505.5	364.4	1.001	4.827	(f)	20	4.090	47.03
/bromocamphor; 0 °C									
Tristearin	891.4	564.6	398.7	1.001	3.652	(f)	20	3.113	18.10
/bromocamphor; 90 °C									
Aluminum/copper	63.54	6.633	44.36	1	1.195	5.964	18	1.196	1.291
Aluminum/magnesium	26.98	15.50	2.772	1	1	1	2	1.015	1.114
Aluminum/zinc	26.98	10.34	-41.6	.9998	.8457	.1873	9.59	.8649	1.114
Copper/aluminum	63.54	6.634	44.37	1	1.195	5.965	18	1.196	1.291
Copper/gold; g	63.54	8.442	-93.4	.9996	.6863	.0232	5	.7028	1.291
Iron/aluminum	55.84	-.529	57.28	1	1.259	10.03	1	1.266	1.252
Iron/copper	55.84	6.260	1.267	1	1	1	.96	.9901	1.252
Lead/gold; g	207.1	20.01	-171	.9993	.5020	.0010	5	.4613	2.302
Lead/mercury; g	207.1	18.02	-35.6	.9998	.8663	.2380	10	.8586	2.302
Lithium/mercury; g	6.939	5.912	-65	.9997	.7697	.0730	2.5	.7465	1.028
Magnesium/aluminum	24.31	13.01	-10.7	.9999	.9575	.6483	1	.9785	1.102
Manganese/aluminum	54.93	8.328	32.40	1	1.139	3.684	.5	1.254	1.247
Nickel/aluminum	58.71	7.349	38.78	1	1.168	4.764	1	1.228	1.266
Oxygen/copper	16	5.816	-35.8	.9998	.8655	.2359	.015	2.747	1.066
Phosphorus/copper	123.8	-83.1	866.7	1.003	32.73	(f)	.04	4.941	1.646
Potassium/mercury; g	39.10	5.504	-34	.9998	.8717	.2535	5	.8818	1.170
Silicon/aluminum	28.08	13.95	-9.10	.9999	.9640	.6930	8	.9722	1.119
Silver/gold; g	107.8	15.69	-182	.9992	.4797	.0006	5	.4849	1.543
Sodium/mercury; g	22.98	3.236	-20	.9999	.9224	.4462	5	.9287	1.096
Tin/gold; g	118.6	21.97	-281	.9988	.3224	1E-5	5	.3569	1.612
Zinc/copper	65.37	21.90	-118	.9995	.6217	.0086	7	.6776	1.300

^aDilute solution; 1 G; h = 1 m.

^bDilute solution; 100 000 G's; h = 1 cm.

^cDilute solution; 1 000 000 G's; h = 1 cm.

^dConc. indicated in 'range' column; 100 000 G's; h = 1 cm.

^e100 000 G's; h = 1 cm.

^fExceeds 10 to the 38th power.

^gObtained from graph.

TABLE III. - KINETICS PROGRAM FOR DIFFUSION IN A GRAVITATIONAL FIELD

```

10 REM GRAV/DIF
11 GOTO 101: REM SET UP PARAMETERS
28 REM LINES 28-31 CALC FLOW; AD=MAX
29 T = T + U: FOR X = 2 TO N: S2 = F(X): S1 = C(X - 1, G) - C(X, G): F(X) = D * (S1 /
  L + SQR ((1 + C(X, G)) * (1 + C(X - 1, G)))) * Y: IF T = U THEN 31
30 IF ABS (F(X) - S2) > AD(X) THEN AD(X) = ABS (F(X) - S2): BD(X) = T
31 NEXT X
32 FOR X = 1 TO N: S2 = C(X, G): C(X, G) = (F(X) - F(X + 1)) / L * U + C(X, G): IF
  T = U THEN 35
33 IF ABS (C(X, G) - S2) > AC(X) THEN AC(X) = ABS (C(X, G) - S2): BC(X) = T
34 S3 = ABS (C(X, G) - C(X - 1, G) - S2 + S1): S1 = S2: IF S3 > AE (X) THEN
  AE(X) = S3: BE(X) = T
35 NEXT X: REM LINES 32-35 CALC NEW CONCENTRATIONS
36 IF T < .9999999 * S * U THEN 29: REM SELECTS VALUES TO BE PRINTED AS
  DETERMINED BY DATA SET
38 HOME : PRINT S$: PRINT "GRAD. --- T="; INT(T): FOR X = 2 TO N: W = (C(X, G) -
  C(X - 1, G)) / (B(X) - B(X - 1)) * (1 + B(X)) / (1 + C(X, G)) * 1000: IF X /
  ST < > INT (X/ST) THEN 40
39 IF W < > 0 THEN PRINT " "; X; "": .1 * INT (W);
40 WW = WW + W: NEXT X: WW = WW / (N - 1): PRINT " AVER)": .1 * INT (WW): WW = 0
41 PRINT "CONC. --- T="; INT (T): FOR X = 1 TO N STEP ST: W = C(X, G) / B(X) *
  1000
42 IF W < > 0 THEN PRINT " "; X; "": .1 * INT (W);
43 NEXT X: PRINT : PRINT E$
44 G(G) = T: G = G + 1
45 FOR X = 1 TO N: C(X, G) = C(X, G - 1): NEXT X
59 READ S
60 IF G < 6 OR ABS (C(N / 2 + 1, G)) < .95 * ABS (B(N / 2 + 1)) THEN 29
70 PRINT S$: PRINT
71 IF XX$ < > "Y" THEN 85: REM BYPASSES ACTUAL GRAD AND CONC DATA PRINT OUT
72 FOR G1 = 1 TO G - 1
73 HOME : PRINT "GRAD. --- T="; INT (G(G1)): FOR X = 2 TO N: W = (C(X, G1) -
  C(X - 1, G1)) / L: IF X / ST < > INT (X / ST) THEN 75
74 IF W < > 0 THEN PRINT " "; X; "": W;
75 NEXT X: FOR X = 2 TO N: WW = WW + W: NEXT X: PRINT " AVER)": W / (N - 1): WW
  = 0
77 PRINT "CONC. --- T="; INT (G(G1)): FOR X = 1 TO N STEP ST: W = 1 + C(X, G1):
  PRINT " "; X; "": W;: NEXT X: PRINT
81 NEXT G1
85 PRINT : PRINT "TIME OF MAX FLOW"
90 FOR X = 2 TO N: PRINT " "; X; "": BD(X);: NEXT X: PRINT : PRINT "TIME OF MAX
  CONC CHANGE": FOR X = 1 TO N: PRINT " "; X; "": BC(X);: NEXT X: PRINT : PRINT
  "TIME OF MAX CONC GRAD"
91 FOR X = 2 TO N: PRINT " "; X; "": BE(X);: NEXT X: PRINT
95 PRINT E$
100 HOME : PRINT "FINISHED": END
101 HOME : REM EVERY QUESTION HAS A DEFAULT VALUE
103 PRINT "ENTER DIFFUSION COEFFICIENT IN CM2/SEC": INPUT D$: D = VAL (D$): IF
  D = 0 THEN D = 1E - 5

```

TABLE III. - Concluded.

```

105 PRINT : PRINT "ENTER THE NUMBER OF G's": INPUT G2$:G2 = VAL (G2$): IF G2
= 0 THEN G2 = 1E5
107 PRINT : PRINT "ENTER BUOYANCY FACTOR IN GRAMS/MOLE": INPUT BU$:BU = VAL
(BU$): IF BU = 0 THEN BU = 100
109 PRINT : PRINT "ENTER HEIGHT IN CM": INPUT H$:H = VAL (H$): IF H = 0 THEN
H = 1
111 PRINT : PRINT "ENTER TEMPERATURE IN CENTIGRADE":H$ = " ": INPUT H$:TEMP =
VAL (H$): IF TEMP = 0 THEN TEMP = 293
112 PRINT : PRINT "ENTER NUMBER OF INCREMENTS": INPUT N$:N = VAL (N$): IF N =
0 THEN N = 20
113 PRINT : PRINT "DO YOU WANT A PRINT OUT? (Y/N)": INPUT H$: IF H$ < > "N"
THEN S$ = CHR$ (4) + "PR#1":E$ = CHR$ (4) + "PR#0"
114 PRINT : PRINT : "DO YOU WANT ACTUAL CONC AND GRAD DATA PRINTED OUT?
(Y/N)": INPUT XX$
115 PRINT : PRINT "ENTER STEP INCREMENT IN PRINT OUT: 1, 2, 3, OR 4":INPUT
ST$:ST = VAL (ST$): IF ST = 1 OR ST = 3 OR ST = 4 THEN 117
116 ST = 2
117 HOME : READ S:A = 1: DIM C(N,15): DIM F(N + 1): DIM B(N): DIM G(15): DIM
AD(N): DIM BD(N): DIM AC(N): DIM BC(N)
118 G = 1: DIM AE(N): DIM BE(N)
119 Y = BU * G2 * 980 / 8.31E7 / TEMP:L = H / N:U = L * L / 2 / D / A
120 U1 = INT ( LOG (U) / LOG (10)):U2 = 10 ^ U1: IF U > 5 * U2 THEN U = 5 *
U2 : GOTO 123
121 IF U > 2 * U2 THEN U = 2 * U2: GOTO 123
122 U = U2
123 FOR X = 1 TO N:Q = Q + EXP (Y * ((X - .5) * L - .5 * H)): NEXT X
124 Q = N / Q:Q = LOG (Q)
125 FOR X = 1 TO N:B(X) = - 1 + EXP (Y * ((X - .5) * L - .5 * H) + Q): IF
B(X) = 0 THEN B(X) = - 1E - 38
127 NEXT X: REM LINES 120-126 CALCULATE EQUILIBRIUM CONCENTRATIONS, B
129 PRINT S$: PRINT "BUOY=";BU;" HEIGHT=";H;" # OF SLICES=";N;" DIFF
COEF=";D;" ";G2;"G's TIME INCREMENT=";U: PRINT
130 PRINT "EQUIL VAL ";;: FOR X = 1 TO N: PRINT " ";X;";";B(X);: NEXT X: PRINT
: PRINT E$
140 GOTO 29
1000 DATA 1,2,5,10,20,50,100,200,500,1000,2000,5000,10000
1002 DATA 20000,50000,100000,200000,500000

```

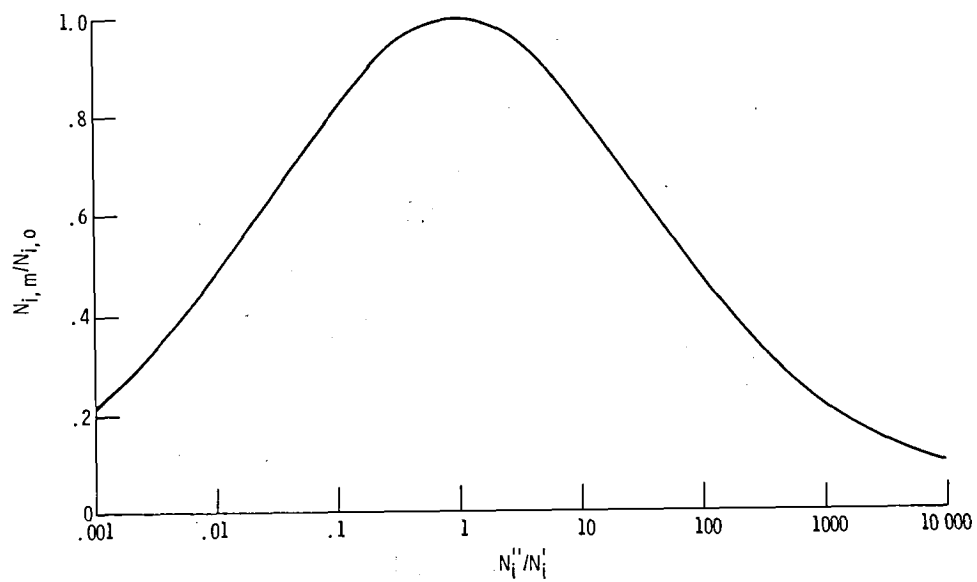


Figure 1. - Ratio of mid-height concentration to initial concentration as a function of N_i''/N_i' at gravitational equilibrium.

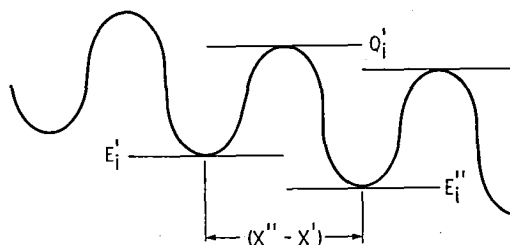


Figure 2. - Model of diffusion in a gravitational field.

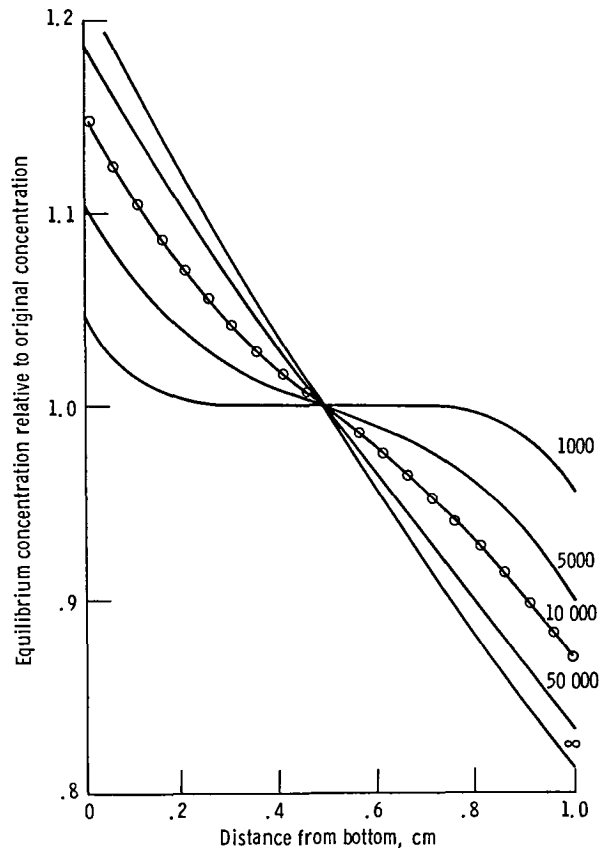


Figure 3. - Predicted concentration profiles of solute at 100 000 G's (time on curve is in seconds; buoyancy factor = 100 grams/cc; h = 1 cm; $D = 10^{-5} \text{ cm}^2/\text{sec}$).

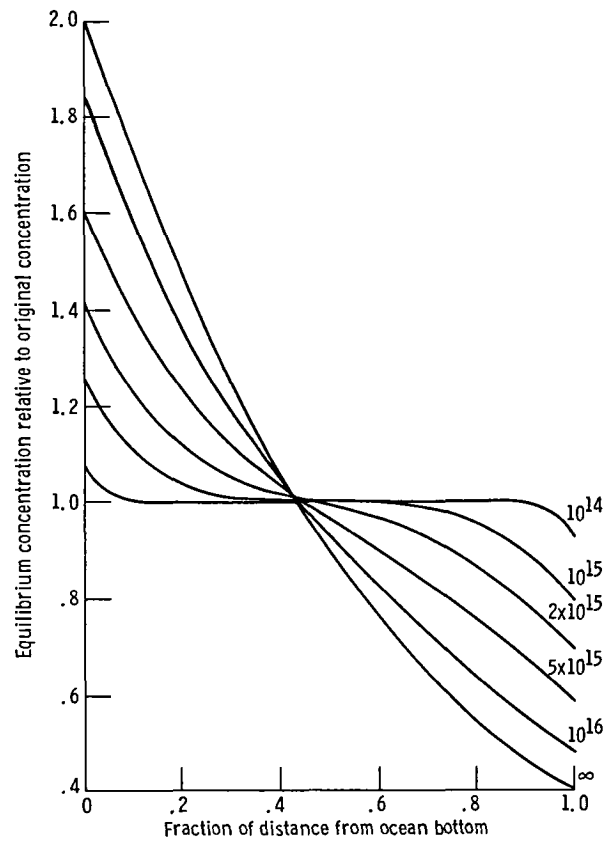


Figure 4. - Predicted concentration profiles of sodium chloride in ocean (time on curves is in seconds).

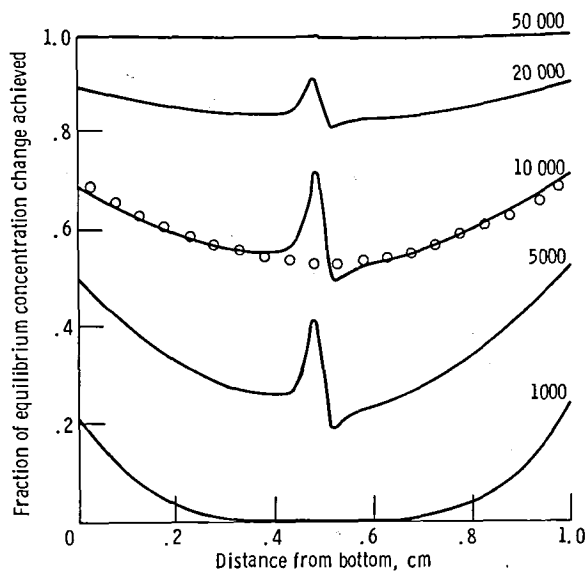


Figure 5. - Profiles of attainment of concentration equilibrium in gravitational field (time on curves is in seconds; $h = 1$ cm; $D = 10^{-5}$ cm²/sec).

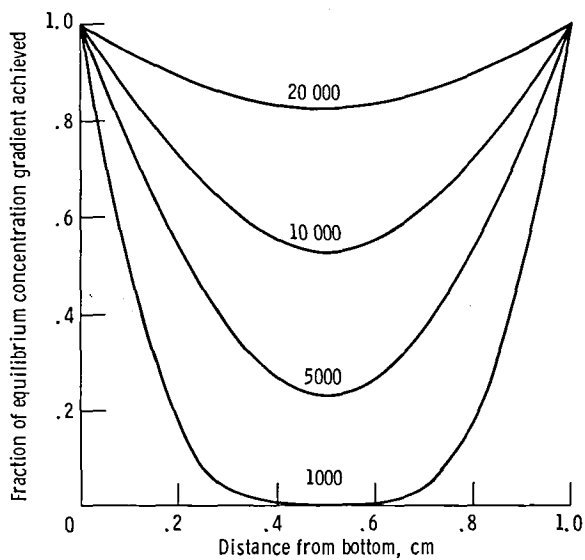


Figure 6. - Profiles of attainment of concentration gradient equilibrium in gravitational field (time on curves is in seconds; $h = 1$ cm; $D = 10^{-5}$ cm²/sec).

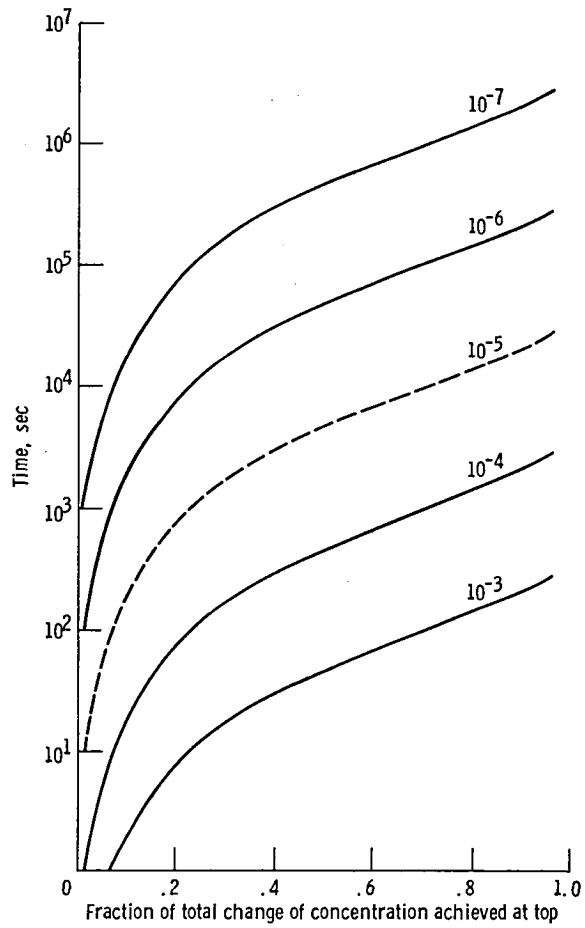


Figure 7. - Time required to approach equilibrium (numbers on curves are D/h^2 in sec^{-1}).

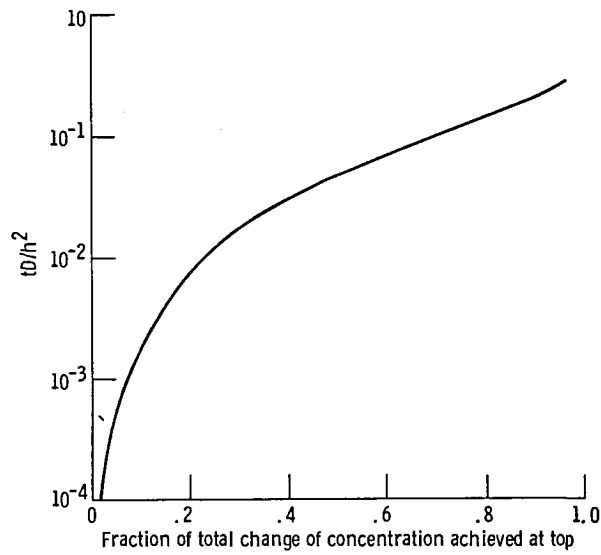


Figure 8. - Time parameter as function of fraction of equilibrium achieved.

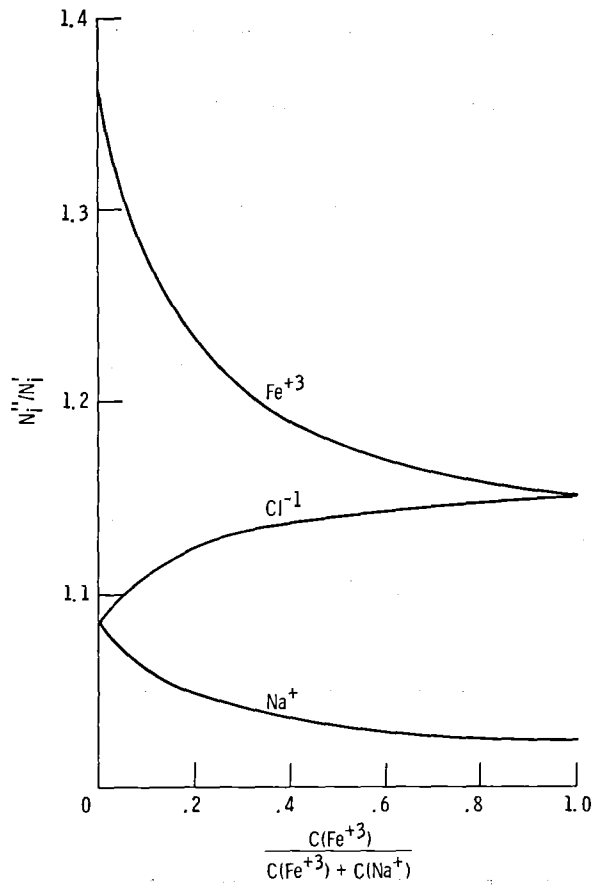


Figure 9. - Concentration ratio in 100 000 G field for 1 cm high column of aqueous solution of NaCl and FeCl_3 .

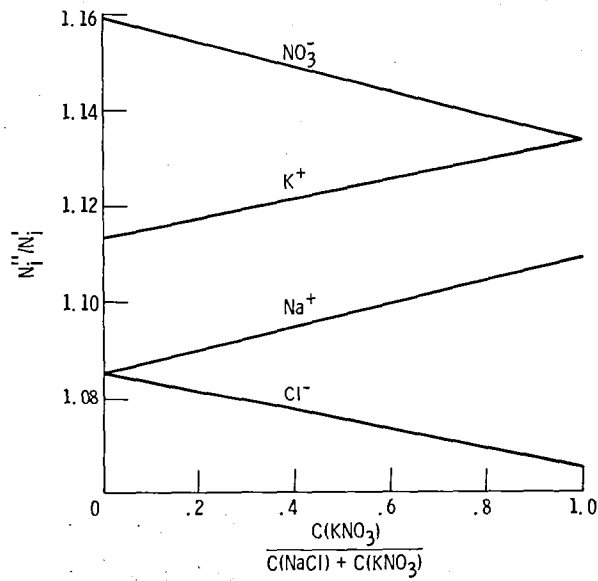
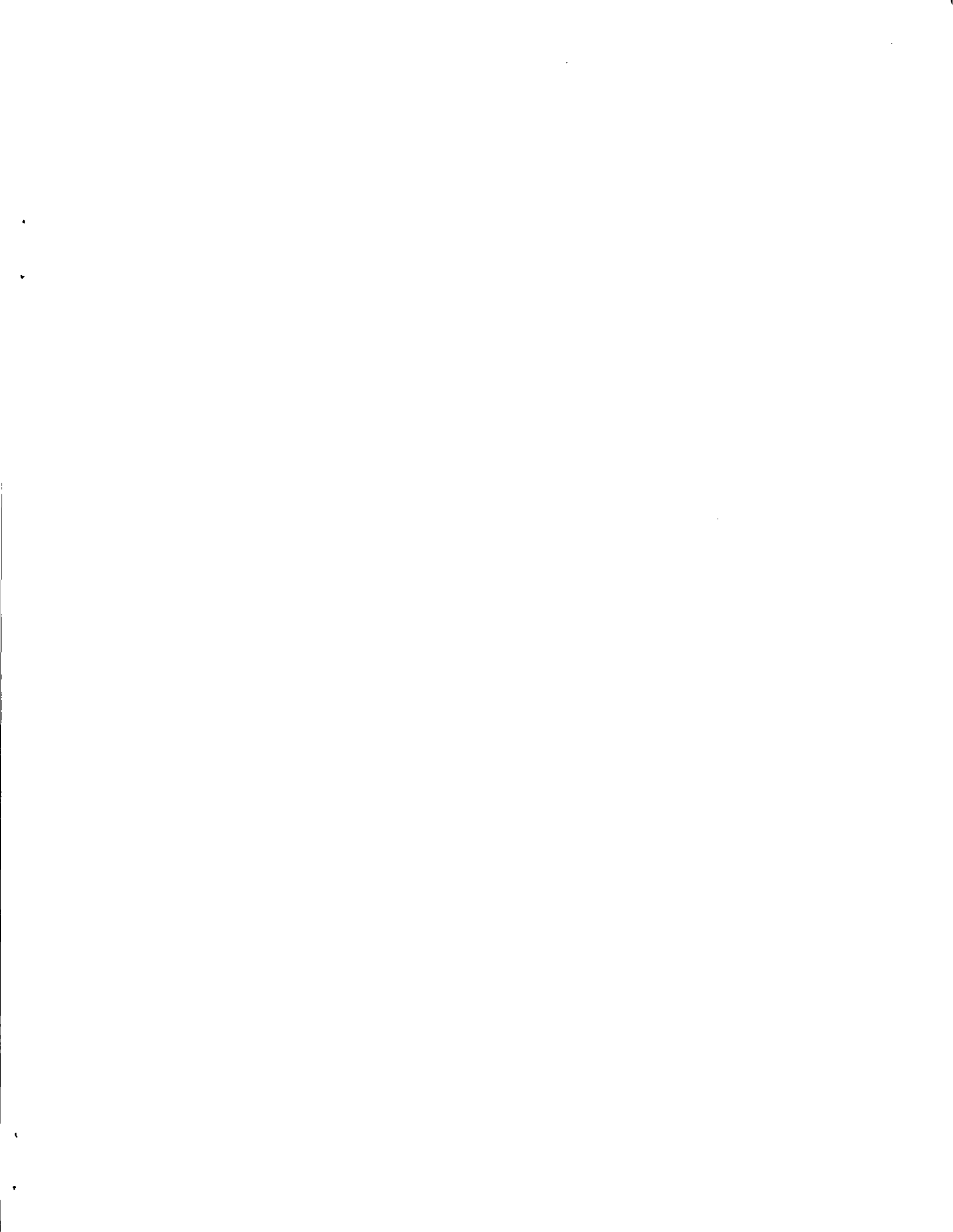


Figure 10. - Concentration ratio in 100 000 G field for 1 cm high column of aqueous solution of Na^+ , K^+ , Cl^- , and NO_3^- .

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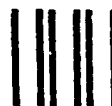
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