$d\eta/d\tau$ can assume for locked-in motion (*9*) occurs when $\eta = 0$, and is

$$|d\eta/d\tau|_{\max} = (\frac{21}{2}\lambda e)^{\frac{1}{2}}$$

With inclusion of the contributions from the first terms on the right-hand side of Eq. 7b, therefore, the values of $d\theta/dt$ for locked-in motion are expected to lie between the limits

$$\left[\frac{d\theta}{dt}\right]_{\max,\min} =$$

$$\frac{3\pi}{T}\left[1 + \lambda\cos\frac{2\pi t}{T} \pm \frac{2}{3}(\frac{21}{2}\lambda e)^{\frac{1}{2}}\right] \quad (10)$$

where we have neglected the term proportional to λe.

The foregoing analysis serves to confirm that locked-in rotational motion with a period approximately 2/3 the period of revolution is dynamically possible. The form of the solution shown in Eq. 7b suggests, however, that observations of the rotation will indicate rates that vary during the course of a planetary year and that, in addition, slower variations of the rotational rate may occur with a period given by

$$T_{\text{lib}} = (\frac{21}{2}\lambda e)^{-\frac{1}{2}} T \qquad (11)$$

when the amplitude (α_0) of this libration is not large. An expression of the form given by Eq. 7b may be useful for interpretation of data obtained by the sequential observation of surface features on the planet. More simply, the *instantaneous* periods—as could be inferred from radar observations—would be (by differentiation of Eq. 7b when the term proportional to λe is neglected)

$$T_{\text{i}} = \frac{2\pi}{d\theta/dt}$$

$$= \frac{2}{3}\left\{1 - \lambda\cos\frac{2\pi t}{T} - \frac{2}{3}\alpha_0(\frac{21}{2}\lambda e)^{\frac{1}{2}} \times \cos\left[(\frac{21}{2}\lambda e)^{\frac{1}{2}}\frac{2\pi t}{T} + \alpha_1\right]\right\} T \qquad (12)$$

for α_0 small, and, for any α_0 compatible with locked-in motion, would lie between the limits obtained from Eq. 10:

$$\left[T_{\text{i}}\right]_{\max,\min} =$$

$$\frac{2}{3}\left[1 - \lambda\cos\frac{2\pi t}{T} \mp \frac{2}{3}(\frac{21}{2}\lambda e)^{\frac{1}{2}}\right] T \quad (13)$$

For favorable values of α_0 a determination of λ may be feasible through observation of the slow libratory motion, with a period close to that expressed by Eq. 11, that is represented by the last term of Eq. 12. If, however, α_0 is very small—as could well result from the action of damping mechanisms—the term

$$-\frac{2}{3}\lambda\cos\frac{2\pi t}{T}$$

in Eq. 12 will represent the larger contribution to the variation of the instantaneous period.

Substitution of the values $T = 87.97/365$ yr, $e = 0.2$, and $\lambda = 5 \times 10^{-5}$, as suggested by Liu and O'Keefe (*4*), into Eq. 11 leads to a libration period $T_{\text{lib}} = 23.5$ yr for small-amplitude variations, in substantial agreement with their computational results. Correspondingly, from the last term of Eq. 13, the maximum variation of the instantaneous period of rotation that could arise from this libratory motion would be approximately ± 0.40 day, in good agreement with recent computational results of Liu and O'Keefe (*10*). It is highly unlikely, of course, that such large variations are now actually occurring, because of the damping that would have resulted from tidal effects.

Although the detailed results presented in this report have been with reference to motion for which the rotation period is close to 2/3 the period of revolution, the existence of other stable modes of locked-in motion should not be overlooked. The possible range of variation for the rotational speed in general will be substantially smaller for the higher-order modes, for reasonable values of the parameter λ, and this feature will have significant implications concerning the magnitude of the damping present at times when the speed of planetary rotation may have been considerably greater than that now observed. Lower limits, which depend on λ, can be set to the rate of decrease of the rotational energy through the agency of damping if the rotational motion has passed through the higher-order modes during the past history of the planet. Similarly, an upper limit can be set on the amount of damping that will permit the rotation to remain locked in to the mode analyzed in this report. Other work (*11*) indicates, moreover, that damping torques acting at present would shift the phase of the periodic solutions presented here, and this result suggests that information concerning the current magnitude of such torques may be inferred from more detailed observation of the rotational motion.

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7. This ignores the (small) effect of the nonuniform rotation (as computed in this paper) upon the orbital motion. Interestingly enough, it leads, most dramatically, to a perihelion motion which contains both a secular term and a term with period $(21\lambda e/2)^{-\frac{1}{2}}T$. These terms are small—of the same order as the perihelion advance present when $A = B \neq C$—even when compared with the general relativistic perihelion advance of 43.8 seconds of arc per century.
8. K. R. Symon *et al.*, *Phys. Rev.* **103**, 1837, 1858 (1956).
9. This result is $2/\pi$ times as great as the corresponding value that would have been inferred from use of $\alpha_0 = \pi/2$ in the solution given by Eq. 7 for the linearized problem. The period of these slow oscillations, moreover, will not be that suggested by the last term in Eqs. 7a and 7b but will approach infinity as the amplitude approaches $\pi/2$.
10. We are grateful for the opportunity to discuss Liu and O'Keefe's work with them, and we appreciate their courtesy in making some of their recent computational results available to us.
11. L. J. Laslett and A. M. Sessler, in preparation.
12. Work supported by the AEC. We thank Penelope A. Collom for assistance with numerical checks.

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Soil-Water Potential: Direct Measurement by a New Technique

Abstract. *Current methods of measuring the potential of water in soil are inadequate. It is proposed to depress the reference free energy of water by a predetermined amount from the standard level of pure free water at atmospheric pressure by use of a solute. The specific free-energy difference of soil water from the depressed reference can be measured as a pressure.*

A long-standing problem in studies of water relations in unsaturated soils is the accurate measurement *in situ* of the potential of soil water. This potential, which is usually measured in units of pressure, is negative with respect to that of the standard reference state: pure free water at atmospheric pressure.

Soil-water relations are usually studied in an agricultural context where the range of water potentials of practical interest for plant growth is very roughly 0 to −15 atm (*1*). Currently available instruments for measuring water potential in this context are inadequate because of limited range and accuracy (*2; 3*, p. 64); they measure either the pressure of water in equilibrium with soil water, or an electrical property of a

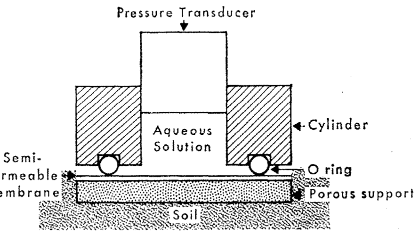

Fig. 1. Basic design (schematic) of instrument for determining soil-water potential.

porous block in hydraulic contact with the soil. We propose a new principle of measurement that promises improved accuracy over the full range of soil-water potentials that is of practical interest in agricultural and other problems.

The specific free energy of water in an aqueous solution is lower than that of pure water under the same conditions, but by application of pressure to the solution the specific free energy of the water can be restored to its value in the pure state. The pressure required to effect restoration is defined as the osmotic pressure of the solution. If pressure less than the osmotic pressure is applied, the specific free energy of the water is increased to a value intermediate between that in the solution and that of pure water.

Thus the addition of a solute provides a convenient means of depressing the specific free energy of water below the standard reference level; with sufficient depression, the specific free energy of water in an aqueous solution can be made less than that in a particular soil.

Let us consider an isothermal system consisting of such a solution physically constrained in a container that is surrounded by unsaturated soil; it is so arranged that water, but not solute, can be exchanged between solution and soil. Water will move from soil to solution, increasing the pressure of the solution until at equilibrium the specific free energy of water is the same throughout the system. In centimeter-gram-second units, the difference between the equilibrium pressure and the osmotic pressure of the solution is numerically equal to the specific free energy of the soil water (*4*); this difference is also a measure of the potential of the soil water. The determination of soil-water potential then reduces to simple measurements of pressures in excess of atmospheric.

In order to apply this principle we are constructing instruments basically similar to the classical osmometer (Fig. 1). So long as a specific free-energy difference exists between the water in the soil and that in the solution, water moves through the semipermeable membrane and its porous support with consequent changes in solution pressure.

A basic factor in design is the quantity of water that must pass through the semipermeable membrane to bring about unit change in solution pressure. This factor must be kept as small as possible in order to minimize (i) change of solution concentration; (ii) soil-water disturbances; and (iii) the time constant of the instrument, which is determined by this factor and by the resistance of the semipermeable membrane and its porous support to water transfer.

A suitable membrane-solute combination appears to be Visking dialysis membrane and polyethylene glycol of molecular weight 20,000 (*5*), but other combinations may prove to be preferable. We have used commercial pressure transducers and others of our own construction. It is generally desirable that the support plate should be finely porous, as water transfer through the plate should be in the liquid phase. In the absence of liquid transfer through the plate, equilibration will be by way of the vapor phase, and in general the instrument's time constant will be increased significantly.

Commonly the soil water will contain solute molecules (different from the basic solute within the instrument) that can pass through the semipermeable membrane. In such instances the instrument indicates not the total water potential but what is now commonly called the matric potential (*3*, p. 14). The instrument can be adapted to measure the total water potential in the presence of soil-water solutes by the deliberate inclusion of a vapor gap within the porous support.

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3 January 1966

Precipitate Formation in the Strontium-Phosphate System

Abstract. *Study of the precipitation process in the aqueous* $Sr(OH)_2$–H_3PO_4 *system, in order to elucidate the phase transformations and the nature of the final solid phases, shows that over much of the range of compositions studied the initial precipitate is poorly crystalline; the x-ray pattern resembles that of strontium hydroxyapatite but has a strontium:phosphorus molar ratio close to 1.3. Within 1 hour the initial precipitate changes to a stable crystalline phase (or phases), with corresponding change, either up or down, in the strontium:phosphorus ratio. At high ratios of* $Sr(OH)_2$ *to* H_3PO_4 *the initial precipitate is* $Sr_3(PO_4)_2 \cdot 4H_2O$*, which then converts to a phase having the x-ray diffraction pattern of strontium hydroxyapatite, but having a strontium:phosphorus ratio that depends somewhat on the initial ratio of* $Sr(OH)_2$ *to* H_3PO_4 *used in the precipitation.*

In studying the titration curve of strontium hydroxide versus phosphoric acid at 38°C, Holt, Pierce, and Kajdi (*1*) found that, when less than one equivalent of strontium hydroxide was added, the curve of *p*H versus amount of $Sr(OH)_2$ was the normal acid-base titration curve; but when more than one equivalent was added precipitation occurred. The curve of *p*H versus equivalents of strontium hydroxide showed one plateau just beyond one equivalent, another between two and three equivalents. The molar ratio of Sr:P in the solid changed from 1.0 at one equivalent to 1.53 at three equivalents of strontium hydroxide.

Their characterization of the solid phase was based on only chemical and microscopic analyses and their understanding of the nature of the various precipitates was consequently incomplete. When two new strontium phosphate phases were discovered (*2*), I tried to clarify the relation between the various solid phases by systematically investigating the $Sr(OH)_2$–H_3PO_4 titration curve, with x-ray diffraction analyses of the solids.

The titration data were obtained by the method of Holt *et al.* (*1*). Various amounts of $Sr(OH)_2$ were added to 100-ml solutions containing 0.002 equivalents of H_3PO_4; each solution was diluted to 200 ml and each reaction flask was sealed and placed on a shaker. One series of experiments was carried out at 24° ± 1°C (except for a rise to