9. T. Sharma and R. N. Clayton, *Geochim Cosmochim. Acta* **29**, 1347 (1966).
10. Useful equilibrium carbon isotope data were sacrificed in order to optimize conditions for oxygen exchange. However, the same techniques employed to obtain the oxygen data could undoubtedly be used for the carbon isotopes.
11. H. C. Urey, *J. Chem. Soc.* **1947**, 562 (1947).
12. J. Bigeleisen and M. G. Mayer, *J. Chem. Phys.* **15**, 261 (1947).
13. J. R. O'Neil and R. N. Clayton, in *Isotopic and Cosmic Chemistry*, H. Craig, S. L. Miller, G. J. Wasserburg, Eds. (North-Holland, New York, 1964), p. 157.
14. J. R. O'Neil, thesis, University of Chicago (1963).
15. W. Compston and S. Epstein, *Trans. Am. Geophys. Union* **39**, 511 (1958); J. R. O'Neil and S. Epstein, in preparation.
16. Supported by NSF grant No. GP 2254 and AEC contract No. AT (04-3)-427. Contribution No. 1396 of California Institute of Technology, Pasadena.
* Present address: U.S. Geological Survey, Federal Center, Denver, Colo.

7 February 1966

Rotation of the Planet Mercury

Abstract. *The equations of motion for the rotation of Mercury are solved for the general case by an asymptotic expansion. The findings of Liu and O'Keefe, obtained by numerical integration of a special case, that it is possible for Mercury's rotation to be locked into a 2:3 resonance with its revolution, are confirmed in detail. The general solution has further applications.*

The recent discovery by Pettengill and Dyce (*1*) that Mercury's rotation is direct, with a period approximately two-thirds of its period of revolution about the Sun, has led to speculation (see Colombo, *2*) that there might be a resonance lock. Liu and O'Keefe (*3*) independently investigated this possibility by numerical integration of the equations of motion and found such a resonance lock to be possible.

If $A < B < C$ are the principle moments of inertia of Mercury, assumed constant, and if C is taken perpendicular to the orbital plane, then the equations of motion governing the rotation of Mercury are, from equation 4 of Liu and O'Keefe,

$$\frac{d^2\psi}{dt^2} + \frac{3}{2}\lambda \frac{\sin 2\phi}{r^3} = 0 \qquad (1)$$

where ϕ is the angular displacement of the principle axis, A, from the direction of the radius vector; $\psi = f + \phi$, f being the true anomaly of Mercury; $\lambda = (B - A)/C$ and r is the distance from Mercury to the Sun; and t is time. Units of mass, length, and time are chosen so that Mercury's mean motion and semimajor axis, and the constant of gravity, are all unity.

Equation 1 can be derived from a Hamiltonian system of two degrees of freedom in the variables ψ, Ψ (conjugate to ψ), ℓ (the mean anomaly of Mercury) and L (conjugate to ℓ), with the equations of motion

$$\begin{aligned} \frac{d\Psi}{dt} &= F^*_\psi, \frac{d\psi}{dt} = -F^*_\Psi \\ \frac{dL}{dt} &= F^*_\ell, \frac{d\ell}{dt} = -F^*_L \end{aligned} \qquad (2)$$

the subscript denoting partial differentiation, and

$$F^* = -L - \frac{1}{2}\Psi^2 + \frac{3}{4}\lambda \frac{\cos 2(f - \psi)}{r^3} \qquad (3)$$

where f and r are considered to be functions of ℓ.

A resonance condition, if it exists, will be due to the extremely slow motion of the angle

$$\psi - \frac{3}{2}\ell$$

and to the small divisors associated with it. Hence it makes sense to isolate this variable by a canonical transformation:

$$\begin{aligned} x_1 &= 2L + 3\Psi, y_1 = \ell/2 \\ x_2 &= \Psi - \frac{3}{2}, y_2 = \psi - \frac{3}{2}\ell \end{aligned}$$

with equations of motion

$$\frac{dx_i}{dt} = F_{y_i}, \frac{dy_i}{dt} = -F_{x_i}, i = 1,2 \qquad (4)$$

and Hamiltonian (dropping terms which do not contribute to Eqs. 4)

$$F = -\frac{1}{2}x_1 - \frac{1}{2}x_2^2 + \frac{3}{4}\lambda \frac{\cos(2f - 3\ell - 2y_2)}{r^3}$$

where f, ℓ, and r are to be considered as functions of y_1.

To treat this equation we make use of von Zeipel's method of averaging, a method closely related to other averaging techniques but especially suited to canonical systems, as described by Brouwer and Clemence (*4*). Moser has given rigorous justification of the use of such methods (*5*).

We introduce a new set of canonical variables, denoted by bars over the corresponding old variables, by means of a determining function

$$S = \Sigma\, \bar{x}_i y_i + S_1 + S_{3/2} + \ldots$$

where $S_n = O(\lambda^n)$, λ being considered a small parameter, and

$$x_i = S_{y_i}, \bar{y}_i = S_{\bar{x}_i}, i = 1,2 \qquad (6)$$

Similarly, the new Hamiltonian, $\bar{F}(\bar{x}_i, \bar{y}_i)$, is developed in a series

$$\bar{F} = \bar{F}_0 + \bar{F}_1 + \bar{F}_{3/2} + \ldots$$

with

$$\bar{F}_n = O(\lambda^n).$$

It is assumed that the new variable $\bar{x}_2 = O(\lambda^{1/2})$. (Incidentally, the choice ascending powers of $\lambda^{1/2}$ is not mandatory but is convenient for present purposes.) Then Eqs. 6 are inserted into the equation expressing the constancy of the Hamiltonian under this transformation,

$$F(x_i, y_i) = \bar{F}(\bar{x}_i, \bar{y}_i)$$

which is expanded in powers of $\lambda^{1/2}$, and terms of like order are compared. The result is a sequence of equations for determining $\bar{F}_n$ and S_n recursively. In this particular case it is possible to choose $\bar{F}$ so that it does not depend on $\bar{y}_1$ (making $\bar{x}_1$ a formal integral of the system) and S so that it is periodic in y_i. The Hamiltonian $\bar{F}$ is also a formal integral, and, according to Moser's work, it is an approximate integral for all time.

Carrying out this process, since $\bar{F}_{3/2}$ happens to vanish, we obtain

$$\bar{F} = -\frac{1}{2}\bar{x}_1 - \frac{1}{2}\bar{x}_2^2 + \frac{3}{4}\lambda \cos 2\bar{y}_2 \times \left\{\frac{1}{2\pi}\int_0^{2\pi} \frac{\cos(2f - 3l)}{r^3}\, dy_1\right\} + O(\lambda^2)$$

The integral can be evaluated straightforwardly by the formulas of elliptic motion and is a function of the eccentricity e alone. It is *not* necessary for e to be a small parameter. For Mercury $e = 0.2056$, and the quantity in brackets is 0.613, so that the new Hamiltonian is

$$\bar{F} = -\frac{1}{2}\bar{x}_1 - \frac{1}{2}\bar{x}_2^2 + 0.460\lambda \cos 2\bar{y}_2 + O(\lambda^2) \qquad (7)$$

Excluding the constant first term and the terms in $O(\lambda^2)$, we recognize that this expression is like the Hamiltonian of a pendulum, with stable equilibria at $y_2 = 0,\pi$ and unstable equilibria at $y_2 = \pm\pi/2$. The limiting period P of the oscillation around the stable equilibria is found to be

$$P_{\text{lim}} = 0.178\ \lambda^{-1/2} \text{ years.} \qquad (8)$$

By standard pendulum formulas, if the maximum value of $\bar{y}_2$ in its oscillation about $\bar{y}_2 = 0$ is ϕ, the period is given by a factor containing an elliptic integral:

$$P = P_{\text{lim}} \left\{\frac{2}{\pi}\int_0^{\pi/2} \frac{d\theta}{(1 - \sin^2\phi \sin^2\theta)^{1/2}}\right\} \qquad (9)$$

For the value $\lambda = 5 \times 10^{-5}$ investigated by Liu and O'Keefe, P_{lim} turns out to be 25.1 years, agreeing with their result of 25 years. They found that the amplitude of oscillation of the instantaneous period was 0.008 days, which corresponds to $\phi \approx 1.2°$, so that Eq. 9 is not needed for this case.

If, through improved accuracy, an oscillation in the rotational period of Mercury could be observed, then from these formulas it would be possible to determine λ and ϕ from the period and amplitude of the oscillation. The period, which would be the best-determined quantity, depends only weakly on ϕ, for moderate ϕ, but strongly on λ, so that the oblateness parameter would be particularly well determined.

Finally, it should be noted that the methods used here are also applicable to other cases of synchronous rotation.

WILLIAM H. JEFFERYS*
University of Texas, Austin

References and Notes

1. G. H. Pettengill and R. B. Dyce, *Nature* **206,** 1250 (1965).
2. G. Colombo, *ibid.* **208,** 375 (1965).
3. H.-S. Liu and J. A. O'Keefe, *Science* **150,** 1717 (1965).
4. D. Brouwer and G. M. Clemence, *Methods of Celestial Mechanics* (Academic Press, New York, 1961).
5. J. Moser, *Nachr. Akad. Wiss. Gött. I. Math. Phys. Kl.* **1962,** 1 (1962).
6. Supported by Alfred P. Sloan Foundation. I thank J. Moser for reading the manuscript.

* Present address: Department of Mathematics, Stanford University, Stanford, Calif.

21 January 1966

Chromium-51 in Sea Water: Chemistry

Abstract. *Chromium-51 introduced into the Pacific Ocean from the Columbia River remains in the hexavalent state. Analysis of this radionuclide in sea water by hydroxide coprecipitation with iron is best accomplished if the chromium-51 is first reduced to the trivalent state.*

Chromium-51 is one of the most abundant radionuclides in effluent coolant waters from nuclear reactors at Hanford, Washington. Because the chemistry of chromium in terrestrial waters is not well known, it is not a simple matter to predict the distribution of Cr^{51} among solution, sediment, and biota. We now present data concerning the chemical form of Cr^{51} in sea water and on the analysis of Cr^{51} in sea water by coprecipitation with ferric hydroxide.

To precipitate certain radioactive trace elements, stable isotopes of the elements in question are usually added as carriers (*1*). Early efforts to recover radionuclides, produced at Hanford, from sea water samples taken off Oregon made use of carrier techniques (*2*). That is, $ZnCl_2$, $CrCl_3$, $CoCl_2$, and $MnCl_2$ were added to samples to assure recovery of Zn^{65}, Cr^{51}, Co^{60}, and Mn^{54} neutron-induced radionuclides known to be present in the Hanford effluent. The metals were removed from sea water by coprecipitation as hydroxides.

We used a similar process in our first tests of Oregon coastal waters, except that we used ferric hydroxide as a bulk precipitate and added lesser amounts of carrier Cr(III), Zn(II), and Mn(II). Gamma-ray analyses of precipitates thus obtained from 560 liters of sea water collected off Newport, Oregon, indicate the possible presence of Sb^{124} for which no carrier was added (Fig. 1, dotted line). In an effort to obtain maximum recovery of this radionuclide, we processed a duplicate sample using the same carriers with the addition of $SbCl_3$. Although no great increase in Sb^{124} recovery occurred, there was a striking gain in yield of Cr^{51} (Fig. 1, solid line). This phenomenon prompted a close examination of the chemistry of Cr^{51} in sea water and the precipitation process itself.

Only the valence states Cr(III) and Cr(VI) need be considered for chromium in surface waters since Cr(II) is unstable in aerated aqueous solution. Chromium from the reactor is introduced to the Columbia River as a hexavalent anion, $Cr_2O_7{}^{2-}$. At the *p*H of river water and in the concentration at which chromium appears, this ion should dissociate to yield $CrO_4{}^{2-}$. Nelson (*3*) found that most of the Cr^{51} in the river remains in solution as an anion, presumably $CrO_4{}^{2-}$. Krauskopf (*4*) calculated that $CrO_4{}^{2-}$ is thermodynamically stable in open ocean water and showed that it is not appreciably removed from sea water by most common mineral surfaces or by plankton.

Trivalent chromium would probably be $Cr(OH)_2{}^{+}$ if in solution, or the hydrous oxide if in the solid phase. Nelson and Cutshall (*5*) concluded that any Cr(III) formed in the river is rapidly sorbed to sediment particles. Curl *et al.* (*6*) reported rapid sorption of Cr(III) to glass beads or plankton from sea water solutions. Johnson (*7*) found that particle-bound Cr^{51} is not displaced by sea water. Thus, Cr(VI) that becomes reduced to Cr(III) is susceptible to sedimentation and is not likely to be found in filtered water samples. However, it seems likely that most of the Cr^{51} entering the ocean in solution will remain in solution as $CrO_4{}^{2-}$ and, indeed, our ability to measure Cr^{51} many kilometers from the river's mouth (*8*) reinforces this hypothesis.

At intermediate values of *p*H Cr(III) will coprecipitate with $Fe(OH)_3$, whereas Cr(VI) will not. Instead, Cr(VI) may be adsorbed and occluded, especially at *p*H values at which ferric hydroxide has a positive zeta-potential ($p\mathrm{H} < 8.3$).

Chromium(III) carrier should not affect the recovery of Cr(VI). On the other hand, Cr(VI) should act as a "hold-back" carrier, and its addition should diminish the yield. If, however, the Cr(VI) is reduced to Cr(III), coprecipitation should be efficient. It seemed probable that the addition of Sb(III) carrier had unexpectedly caused this reduction, the yield thus being enhanced.

The following experiments were designed to resolve this point. In the laboratory Cr^{51} spikes, as Cr(III), were added to filtered sea water, and the yields checked with and without carriers. This was repeated for Cr^{51} as Cr(VI), plus additional tests with Sb(III) and Sn(II) as reducing agents. Results (Table 1) show that recovery of Cr(III) by coprecipation with $Fe(OH)_3$

Table 1. Recovery of Cr^{51} spikes by $Fe(OH)_3$ precipitates in the laboratory (percent).

Carrier added			Reducing agent added
None	Cr(III)	Cr(VI)	
		Chromium(III)	
98.3	99.1	98.1	
98.3	95.2	99.1	
		Chromium(VI)	
72.4	38.4	1.9	99.5 [Sb(III)]
27.3	15.9	2.2	99.6 [Sn(II)]

Table 2. Chromium-51 recovered from sea water samples by $Fe(OH)_3$ precipitates (pc/liter). All locations were 44°39′N.

Carrier added			Reducing agent added
None	Cr(III)	Cr(VI)	
		June 1965; 125°12′W	
13.4	24.7	4.7	53.3 [Sb(III)]
	8.2		59.1 [Sb(III)]
		August 1965; 125°38′W	
5.8	2.0		9.2 [Sb(III)]
			10.2 [Sn(II)]
		August 1965; 125°02′W	
		0.9	23.5 [Sb(III)]