ciency, optimized spectral filtering, higher photomultiplier quantum yield, and electronic correlation filtering (*11*) matched to the transit time of a molecule through the laser beam. On the basis of reasonable estimates for signal-to-noise improvements, it may be possible to detect a single molecule passing through the probed volume (*5*). This would be a significant improvement in laser-induced fluorescence detection limits. Single-molecule detection limits also provide the ultimate in sample quantitation wherein uncertainties are dominated by counting statistics in the number of molecules processed.

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12 October 1982

Dynamical Consequences of Orthohydrogen-Parahydrogen Disequilibrium on Jupiter and Saturn

Abstract. *The Voyager observation of high zonal flow speeds (about 400 meters per second) in the atmosphere of Saturn has raised fundamental questions about the flow on both Jupiter and Saturn. One possibility is that the flow is extremely deep, perhaps extending through the planet. Another is that the flow is confined near the cloud tops and is associated with very strong buoyancy contrasts. It is demonstrated that the heat of conversion from parahydrogen to orthohydrogen can provide buoyancy contrasts of the required magnitude, and a feedback mechanism is proposed to couple the heat of conversion to the flow dynamics.*

Jupiter and Saturn have internal heat sources whose strengths have been well determined by Voyager spacecraft measurements (*1, 2*). In both cases the energy release is large enough that the interiors should be convective but small enough that, according to conventional theories of convection, the temperature (T) fluctuations are extremely small (*3*), with the fractional change $\delta T/T \sim 10^{-6}$. The simplest conventional treatment of convection is the mixing length theory presented in stellar structure textbooks (*4*), and its most severe test is in application to the sun. There it successfully predicts the observed length scale and time scale of the photospheric granulation (to an order of magnitude, which is all it attempts).

But the simplest ideas fail on Jupiter and Saturn. First, the strong long-lived mean zonal flows detected by the Voyager experiments (*5, 6*) are strikingly at variance with the small-scale turbulence that would be expected. Second, and more quantitatively, it can be inferred from the observed velocities that the temperature fluctuations associated with motions are much larger than theory predicts (unless there is a special geometry to the flow field; see point 3 below). In light of this discrepancy it is important to examine the thermodynamics of the mixtures that compose these atmospheres and to reach an understanding of how they differ from the simple fluids assumed in ordinary convection theory. Those fluids are in local thermodynamic equilibrium, composed of a single constituent, and buoyancy is therefore proportional to heat content. In this report we show that lack of thermodynamic equilibrium between orthohydrogen and parahydrogen in the outer planets can lead to buoyancy effects in their atmospheres that may be large enough to explain the observations. Massie and Hunten (*7*) recently examined equilibration rates and found that they are slow, of the same order as the expected dynamical time scales, although exact rates remain an important uncertainty.

There are, of course, other differences between Jupiter or Saturn and the sun. A key one is the latitudinal distribution on the planets of external heating due to insolation, which energetically is the same order of magnitude as the internal heat. The geometry of the flow may be determined by this boundary condition while the amplitude of buoyancy contrasts is determined by the thermodynamics; we focus in this report on the latter.

How do the observations indicate large temperature fluctuations on Jupiter and Saturn? Steady atmospheric flows on rotating planets are associated with horizontal pressure gradients. In a fluid planet these pressure gradients cannot be produced mechanically by simple accumulation of excess atmospheric mass over certain locations, since there is no rigid surface to support the weight. Instead, there must be horizontal temperature contrasts to puff up different atmospheric columns by different amounts so that, for example, if there is no horizontal pressure gradient between the bases of two columns then one will exist between the tops. Specifically, the change of zonal wind u with height is related to the latitudinal temperature gradient $\partial T/\partial y$ by (*8*)

$$u(p_1) - u(p_2) = \frac{R}{f}\int_{p_1}^{p_2} \frac{\partial T}{\partial y}\frac{dp}{p} \qquad (1)$$

where p_1 and p_2 are the atmospheric pressures at two different levels, R is the gas constant, f is the Coriolis parameter, and the temperature gradient is evaluated along a surface of constant pressure. Assume that the observed dynamical regime is confined to a depth of N pressure scale heights (e-foldings of pressure) below the observed clouds. Then Eq. 1 tells us that to an order of magnitude

$$\delta T \sim \frac{fL}{NR}\, U \qquad (2)$$

where L is the observed horizontal scale of wind variation and U is the wind speed. This is the relationship that provides an estimate of temperature contrasts. In the following discussion we will adopt for both planets $f = 1.76 \times 10^{-4}\ \text{sec}^{-1}$ (corresponding to about 30° latitude), L = 2000 km (corresponding to a latitudinal wavelength of the zonal flow oscillation of about 13,000 km), and $R = 4.16\ \text{J g}^{-1}\ \text{K}^{-1}$ (corresponding to hydrogen). These values are sufficiently accurate for the arguments presented below, and a single set of parameters for both planets will help later to display clearly the changes between the two in hydrogen disequilibrium.

The following points are important.

1) As the Voyager imaging team pointed out (*6*), the high flow speeds on Sat-

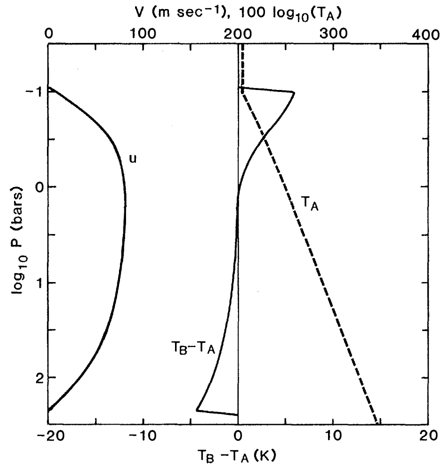

Fig. 1. Model with simulated Jovian stratosphere. Curve T_A illustrates the mean thermal structure. Curve $T_B - T_A$ displays on an expanded scale the temperature difference between profiles following adiabatic relationships for orthohydrogen abundances frozen at the equilibrium values corresponding to the stratosphere temperature and the high temperature of deep layers, respectively. The wind profile is calculated as explained in the text.

urn imply very large temperature variations if $N \sim 1$. With $U = 400$ m sec^{-1}, Eq. 2 gives $\delta T \sim 35$ K, or a fractional temperature change $\partial T/T \sim 0.23$, assuming $T \sim 150$ K at cloud level. There is no evidence for such large contrasts, nor have there been theoretical proposals for the origin of such large contrasts, and the experimenters conclude that the flow regime must be deep, with $N \gg 1$.

2) On both planets, even if N is large enough that the flow penetrates deep into the planetary interior, the temperature contrasts are still larger than simple mixing length theory would predict. Equation 2 involves the ideal gas approximation and is valid only to a depth where $p \sim 1000$ bars. Since cloud level is at $p \sim 1$ bar, this gives $N \sim \ln(1000) \sim 7$ and $\delta T \sim 5$ K. At the same depth, mixing length theory predicts $\delta T \sim 10^{-3}$ K [for example, see (*3*)]. The large discrepancy remains if deeper levels with nonideal gas behavior are considered.

3) There is a way out of the difficulty if the flow extends all the way through the planet along cylindrical surfaces parallel to the rotation axis. In this case Eq. 1 is not relevant. If the zonal flow is uniform along such surfaces then there need not be any temperature perturbations at all (*9*). A motion field with such a pattern has been suggested by Busse (*10*), but a complete theory does not yet exist.

In summary, either there are energy transformations that lead to much larger buoyancy effects than occur in ordinary convection or there is a special geometry to the flow field. Release of latent heat at cloud condensation levels appeared to be a promising energy transformation process (*3*) until the Voyager imaging data revealed the strength of flows on Saturn. The largest effect would come from the presumed water clouds beneath the visible ones, but as the experimenters point out (*6*), their influence is probably insufficient. On the other hand, there are also apparently difficulties with the cylindrical geometry hypothesis, since features such as Jupiter's great red spot are not reflected in both hemispheres.

Lack of thermodynamic equilibrium of the ratio of orthohydrogen to parahydrogen could provide an energy transformation mechanism leading to large buoyancy differences. Such disequilibrium has been suggested by Smith (*11*) and Massie and Hunten (*7*), who mentioned that dynamical consequences would exist. Effects would be most pronounced if equilibration time lags were of the same order as the fluid dynamical time scales. Orthohydrogen (parallel proton spins) and parahydrogen (antiparallel) are constrained to occupy only odd and even molecular rotation levels, respectively, and therefore have different internal energies and specific heats. The differences are large at the low temperatures encountered on the outer planets (the characteristic temperature corresponding to the lowest rotational level of the hydrogen molecule is about 87 K). The properties of orthohydrogen and parahydrogen are discussed in standard statistical mechanics texts (*12*). The thermodynamic equilibrium fraction of orthohydrogen varies from 0.75 at high temperatures to zero at low temperatures.

To illustrate the magnitude of the buoyancy effects that could arise, we calculated model atmospheric structures for different assumed vertical distributions of ortho/para ratio. For simplicity we assume pure hydrogen. The model atmosphere consists of an isothermal stratosphere overlying an adiabatic troposphere, a structure qualitatively similar to that of Jupiter and Saturn (*13*). We next envisage that at one location (called A) on the planet the adiabatic troposphere follows a $T(p)$ profile determined by the specific heat of a mixture that is 0.75 orthohydrogen, that is, that the mixture is "frozen" with the composition determined by high-temperature equilibrium. At another location (called B, at a different latitude from A), the structure is assumed different in two respects: the tropopause (stratosphere-troposphere

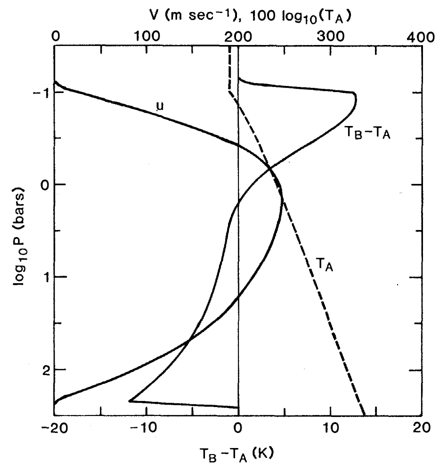

Fig. 2. As in Fig. 1, but with a colder stratosphere to simulate Saturn.

interface) is higher, and the tropospheric $T(p)$ profile follows an adiabat determined by a mixture with an orthohydrogen fraction frozen at the stratospheric equilibrium value. Since this corresponds to a lower temperature, the ortho fraction is smaller than 0.75. This leads to a larger specific heat (*12*) and consequently a slower increase of temperature with depth than in the adiabatic troposphere at A. In Eq. 1 we then evaluate a wind speed by approximating $\partial T/\partial y = (T_B - T_A)/L$.

Results are illustrated in Figs. 1 and 2 for cases with stratosphere temperatures of 110 and 80 K, chosen to represent Jupiter and Saturn (*13*). In each case we place the tropopause of profile A at a pressure of 100 mbar, roughly in agreement with observation. The only other free parameter is the tropopause height assumed for profile B. Since it is higher (at a lower pressure) than that for profile A, we have $T_B > T_A$ in the upper troposphere. But since T_B increases more slowly with pressure than T_A, a crossover can occur. This crossover point moves deeper as the difference between the two tropopause heights increases, and in fact moves to infinite depth for a finite tropopause separation because the ortho and para specific heats begin to differ very little when the temperature exceeds about 300 K.

We have displayed cases just short of this limiting situation, but close enough to it so that the structure near the tropopause is insensitive to the precise crossover depth. This requires the crossover to be at least a few scale heights deep. Finally, since $T_B > T_A$ just below the tropopause and $T_B < T_A$ at greater depth, we can choose the base of the whole system such that the vertical integral of $\partial T/\partial y$ (Eq. 1) vanishes. The wind profiles then show a maximum at the temperature crossover point and drop to zero at the stratosphere base and at the bottom of the model atmosphere.

Figures 1 and 2 show T_A as a function of depth, and on an expanded scale the difference $T_B - T_A$, which is only on the order of 5 K for the Jupiter model and 10 K for the Saturn one. The wind maxima occur near the 1-bar pressure level and are about 80 m sec^{-1} for Jupiter and 250 m sec^{-1} for Saturn. These speeds are in rough agreement with observation. In particular, these results support the hypothesis of a relatively shallow dynamical regime on both planets, while offering an explanation for the differences between the two planets.

There has been no attempt in this construction to develop a self-consistent flow theory, but a feedback mechanism is suggested by the results. The pairs of temperature profiles (T_A, T_B) exhibit the magnitude of temperature differences which disequilibrium might cause. For their existence a downward flow would probably be required at location B, and a process analogous to conditional instability in the terrestrial atmosphere (*7*) is clearly possible. The initial motion would require energy to overcome unfavorable buoyancy, but a threshold would be passed after a certain displacement, beyond which buoyancy would be favorable to augment the motion.

The time scale for overturning would need to be on the same order as that for orthohydrogen-parahydrogen equilibration. The latter remains a pivotal unknown in these considerations. The equilibration time is very long at low temperatures in clean hydrogen gas (*14*), in excess of 10^7 seconds. The rate in the atmospheres of the outer planets is probably determined by the catalytic action of aerosols (*7*), whose abundance and composition are as yet unknown. This question needs work. Observations to date are consistent with thermal equilibrium (*11, 15*), but the uncertainties are large and horizontal resolution has been either nonexistent (whole-disk observations) or barely sufficient to resolve the scales of interest (Voyager infrared spectrometer observations). Disequilibrium could be confined to narrow updraft and downdraft areas.

Note added in proof: It now appears that the Voyager infrared data for Jupiter may indeed indicate significant disequilibrium (*15*).

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23 April 1982; revised 9 July 1982

Abyssal Water Carbon-14 Distribution and the Age of the World Oceans

Abstract. *The carbon-14 distribution in the abyssal waters of the world oceans indicates replacement times for Pacific, Indian, and Atlantic ocean deep waters (more than 1500 meters deep) of approximately 510, 250, and 275 years, respectively. The deep waters of the entire world ocean are replaced on average every 500 years.*

The Geochemical Ocean Sections Study (GEOSECS) program, initiated in 1971, was designed to inventory the chemical constituents in the world oceans. Such an inventory can be used for baseline studies of future chemical changes and for the investigation of large-scale oceanic transport and mixing processes. An important component of the GEOSECS program was the ^{14}C subprogram. Twenty-two hundred samples were collected and extracted on board at 124 stations, of which 39 were in the Atlantic Ocean, 44 in the Pacific Ocean, and 41 in the Indian Ocean. These oceans were, respectively, sampled during the years 1972–1973, 1973–1974, and 1977–1978. The ^{14}C activities (*1*) of the samples were determined with an accuracy of 4 per mil at the University of Miami (H.G.O.) and the University of Washington (M.S.). The laboratory measurements were completed in 1980, and we present here a comparison of the deepwater ^{14}C concentrations of the three oceans.

The ^{14}C distribution of the carbon species in the deep ocean is influenced by many processes. Bottom-water formation in the North Atlantic and the Weddell Sea provides a direct input of surface-water ^{14}C. Additional input of ^{14}C to the deep sea can occur by transport along isopycnal surfaces and by vertical mixing in the main oceanic thermocline. An addition of CO_2 and ^{14}C is provided by the dissolution of carbonate skeletons and the oxidation of organic materials from sinking particles. Mixing between laterally moving water masses and up-

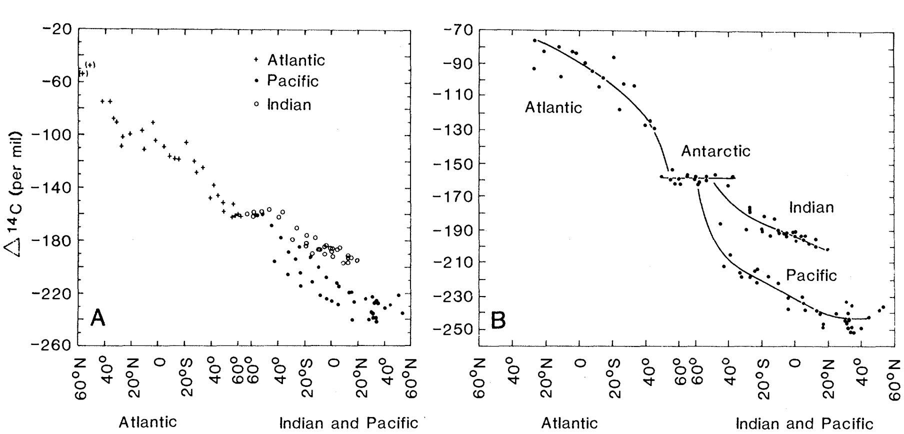

Fig. 1. (A) Average $\Delta^{14}C$ values of waters below a depth of 1500 m for Atlantic, Pacific, and Indian ocean GEOSECS stations. The bracketed points near 60°N in the Atlantic are influenced by nuclear bomb ^{14}C. The southern boundary of the circumpolar current is taken at 65°S. Circumpolar waters, south of 50°S, have nearly uniform $\Delta^{14}C$ values. (B) The $\Delta^{14}C$ values of the cores of North Atlantic, Pacific, and Indian ocean deep waters. The oldest waters are encountered near 40°N in the Pacific Ocean.