SIXTH RAREFIED GAS DYNAMICS

THE ROLES OF KINETIC THEORY AND GAS-SURFACE INTER-ACTIONS IN MEASUREMENTS OF UPPER-ATMOSPHERIC DENSITY

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The roles played by kinetic theory and gas-surface interactions in the inter-pretation of measurements made by mass spectrometers, pressure gauges, and satellite drag are discussed. The effect of adsorption is analyzed in detail. A resolution of the discrepancies between drag and instrumental measurements is proposed, taking into account the corrections for adsorption, gauge calibration, and chemical reactions of atomic oxygen.

1. Introduction

Nearly all measurements of the density of the neutral atmosphere above 100 km have been made in one of the following ways:

1. The air molecules were ionized and the ion currents measured in a mass spectrometer (1) or pressure gauge (2).

2. The drag force or torque on a body was inferred from tracking data (3) or spin-rate measurements (4), or measured by an accelerometer (5).

3. The extinction (or absorption) of solar ultra-violet radiation (6) or X radiation (7) by atmospheric gases was measured.
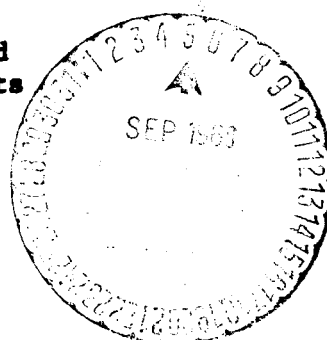
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There are systematic differences among the densities measured at the same place and time by the various methods (1,8-11) so it is a matter of some urgency to investigate the uncertainties associated with each method. Densities measured by methods 1 and 2 depend strongly on what is known or assumed about kinetic theory and gas-surface interactions. Method 1 will be discussed in the present paper, and method 2 will be discussed in a companion paper with G. S. Reiter (12). Method 3 depends on the absorption cross sections of atmospheric gases. The problems associated with the UV cross sections, including their rapid variation with wavelength and, hence, their apparent variation with altitude, have been studied by Hinteregger and his group (6,8). The apparent variation of the x-ray cross sections near 180 km has been observed by Moe, et al.(13). The measurement of cross sections is a spectroscopic problem (14), so it will not be discussed further.

2. Mass Spectrometers and Pressure Gauges

A conventional mass spectrometer or pressure gauge consists of an inlet, a chamber in which molecules reach thermal equilibrium, an ionizing source, and a system which measures currents. Mass spectrometers can measure density and composition, day or night, with a spatial resolution of a few km (15), so they will ultimately be the instruments used to make precise atmospheric measurements; however, mass spectrometers are complicated devices in which many processes occur, and each process can introduce errors into absolute measurements. The possible sources of error in conventional mass spectrometers and pressure gauges include:

1. Calibration (10,16)
2. Decay of sensitivity with time (17)
3. Inlet transmission (18,19)
4. Dissociation (15)
5. Chemical reactions of atomic oxygen (15,20,21)
6. Adsorption (22)

Items 1, 5, and 6 are likely to be major sources of error. In addition, item 3 could be important for rockets near peak altitude. In this paper we shall concentrate our attention on item 6, adsorption, but at the end of the

paper we shall point out how a combination of errors
1, 5 and 6 would explain the disagreements between
instrumental measurements and the densities inferred
from satellite drag.

The effects of adsorption are commonly observed in
spaceborne instruments (23,24,25) but not included in the
analysis of the data. So far, only one preliminary
analysis of the effect of adsorption has been published
(22), so we propose to present a more detailed analysis
of the problem here. This analysis refers to effects
observed in conventional instruments. There also exists
a "nude" mass spectrometer, which lacks the chamber. The
nude mass spectrometer has an additional problem: Thermal
accommodation is incomplete in this instrument. In the
past, data from nude mass spectrometers have been reduced
by assuming the accommodation coefficient to be either
zero or unity, as has been pointed out in the papers of
Mauersberger, et al.(26) and Hedin and Nier (21). A
theory in which partial accommodation and chemical re-
actions are included is presently under development and
will be presented elsewhere.

3. Rocket-Borne Pressure Gauges and Mass Spectrometers

The differential equation which is customarily used
to describe the pressure within the chamber of a rocket-
borne pressure gauge or mass spectrometer can be written

$$\frac{V}{kT} \frac{dp}{dt} = \frac{A_o n_o C_\infty}{2\sqrt{\pi}} F(s \cos\psi) - A_o \mu \qquad [1]$$

where p is the pressure inside the gauge, V is its vol-
ume, T its temperature and A_o the area of its orifice;
k is Boltzmann's constant, t is the time, n_o is the number
density of molecules in the ambient air, C_∞ the speed of
the rocket, and μ is the number of molecules which strike
an area of 1 cm^2 in the gauge from one side in one second.
The function F (s cos ψ) depends on the speed ratio, s,
and the angle ψ between the velocity vector and the normal
to the orifice.

Equation [1] has a well-known solution in terms of
error functions (15). According to this solution, p is
negligibly small when the orifice points downstream;
whereas, in fact, p never is negligibly small. The con-
ventional solution to this dilemma (27) is to subtract

the minimum pressure observed during the spin cycle ("the background") from all other readings, and use this difference, Δp, in place of p in the solution of Eq. [1]. Presumably the physical reasoning behind this step is the assumption that the background is caused by outgassing (desorption of gases present at launch) and is unrelated to the ambient atmosphere. Certainly, outgassing does occur, but if it were the only source of background gas, then the background would continually decrease with time during a rocket flight. An examination of pressure histories during rocket flights reveals that the background does decrease during the upleg and part of the downleg, but then increases continuously during the remainder of the downleg (see Figure 8 of reference 23 and Figure 3 of reference 11). The obvious conclusion is that net adsorption is occurring during part of the rocket flight.

4. Satellite-Borne Instruments

A physically simpler situation occurs in the case of a satellite-borne pressure gauge or mass spectrometer. After it has been in orbit a day or two, the original outgassing has been completed (28), so the net amount of gas adsorbed during a spin cycle is zero, except for a slight amount corresponding to the change in the height of perigee during the spin period (usually about 1 sec). Nevertheless, a significant background persists (see Figure 1, which was taken from reference 24). In order to treat this situation, it was necessary (22) to add two more terms to the differential equation [1]. Assuming that the adsorptive behavior can be described by Langmuir's theory (29), the complete differential equation is:

$$\frac{V}{kT} \frac{dp}{dt} = \frac{A_o \, n_o \, C_\infty}{2\sqrt{\pi}} F \, (s \, \cos\psi) - A_o \, \mu + A_w \nu\theta - A_w \, (1-\theta) \, \alpha\mu, \qquad [2]$$

where A_w is the area of the inside walls of the instrument, θ is the fractional surface coverage, α is the sticking probability, and ν is a constant representing the number of molecules which would be desorbed per second from 1 cm^2 which was coated with one monolayer. The

four terms on the right hand side of Eq. [2] represent
the rate of change of the number of molecules in flight
in the chamber because of influx, efflux, desorption, and
adsorption, respectively.

A perturbative analysis of the effect of adsorption
in producing the background in the Redhead pressure gauge
aboard Explorer 17, assuming that the atmosphere consists
of a single constituent, has been published (22). A
rigorous solution of Eq. [2] has now been obtained, by
employing numerical integration. The absolute values of
the four terms on the right hand side of Eq. [2] are
shown at the top of Figure 2. The pressure, which is
proportional to the time integral of the sum of the four
terms appears below, and the pressure which would have
been measured without adsorption is shown dashed.
In performing the numerical integration the initial con-
ditions were chosen when the orifice pointed downstream.
The initial pressure was $p = 4.8 \times 10^{-8}$ torr and the
initial surface coverage was $\theta = 2 \times 10^{-4}$. The parameters
used in Figure 2, $\alpha = 3 \times 10^{-3}$ and $\nu = 1.2 \times 10^{15}$, were
selected because they caused the pressure and coverage to
return to their initial values after one complete cycle.

The important point to notice is that the peak
pressure with adsorption is lower than the peak pressure
without adsorption, although the ambient number density
is the same. When the minimum pressure is subtracted
from the maximum, in the conventional manner (27), the
ambient number density is underestimated by 34%. Even
after this correction, the density measured by the pres-
sure gauge is still only half that deduced from orbital
decay. The only significant source of uncertainty in
deriving densities from satellite drag in the altitude
range 250-300 km is the drag coefficient. It is unlikely
to be in error by more than 15% (10,30), so the densities
derived from drag data are known to this accuracy. The
remaining discrepancy between drag and instrumental
measurements is probably caused by chemical reactions of
atomic oxygen within the instruments (20,31), and by cal-
ibration errors of the instruments (10,16).

5. Resolution of the Discrepancies Between Drag and
   Instrumental Measurements

We propose to resolve the discrepancies between drag
and instrumental measurements by taking into account

several of the physical processes described above. The extensive collection of measurements from Explorer 17 indicated that the density measured by orbital decay was nearly 2.5 times as large as that deduced from the pressure gauges at altitudes near 280 km. We would multiply the gauge measurements by 1.34 to correct for adsorption, and by approximately 1.2 to correct for collisions between nitrogen and mercury vapor affecting the McLeod Gauge calibration (10,32). This still leaves a discrepancy of 2.5/1.61 = 1.55, which we attribute to the chemical reactions of atomic oxygen discussed by von Zahn (20) and Niemann and Kennedy (31). The compounds formed are presumably less efficiently measured by the gauges. (Cook (10) quotes private communications from A. O. Nier and N. W. Spencer giving experimental evidence of loss of atomic oxygen in enclosed instruments.) A possible alternative explanation of the remaining discrepancy of 1.55 is the suggestion of Friedman (16) that the indirect calibration of atomic oxygen introduces a systematic error through the ratio of absorption cross sections which is employed.

Evidence that gauges incorrectly measure the amount of atomic oxygen is furnished by the gauge data from the Russian Geophysical Rocket and Sputnik 3, which have been compared with drag measurements by Cook (10). The discrepancies between gauge-derived densities and drag-derived densities for these two spacecraft are quite different functions of altitude, because one was aloft at sunspot minimum and the other at sunspot maximum. However, within the experimental accuracy, the discrepancies are the same monotonic function of the mean molecular mass of the atmosphere, as given by the CIRA model. Where the ratio of atomic oxygen to molecular nitrogen is near unity, the discrepancy is small, but where the ratio is large, the discrepancy becomes large also. The obvious conclusion is that only part of the ambient oxygen is being measured, either because of loss mechanisms or incorrect calibration of the instruments for atomic oxygen.

In this paper we have described several phenomena, involving kinetic theory and gas-surface interactions, which can be of importance in interpreting instrumental measurements of atmospheric properties. A better understanding of these processes will enable mass spectrometers and pressure gauges to fulfill the promise inherent in their flexibility and sensitivity.

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Acknowledgments

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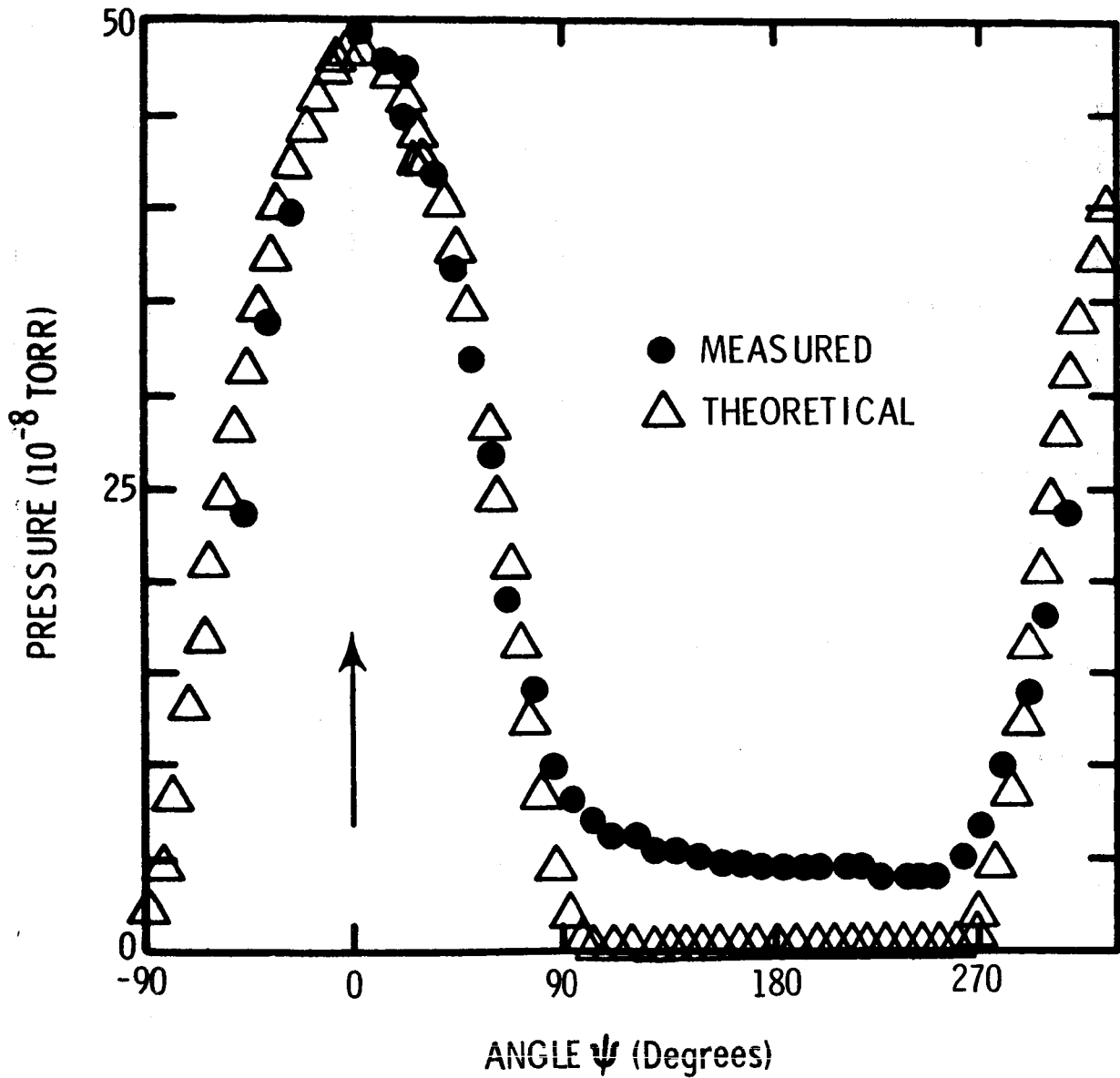## List of Figures

FIGURE 1. REDHEAD GAUGE PRESSURE
(AFTER NEWTON, ET. AL.)

FIGURE 2. PHYSICAL PROCESSES CONTRIBUTING TO GAUGE PRESSURE