DOUGLAS PAPER 4820
MAY 1968

A NEW METHOD OF DETERMINING THE MEAN MOLECULAR MASS

K. MOE

Presented to
Third National Conference on Aerospace Meteorology
New Orleans, Louisiana
6-9 May 1968

DOUGLAS MISSILE & SPACE SYSTEMS DIVISION

MCDONNELL DOUGLAS
CORPORATION

A NEW METHOD OF DETERMINING THE MEAN MOLECULAR MASS

Kenneth Moe
Space Sciences Department
Douglas Aircraft Company
Santa Monica, California 90406

1. INTRODUCTION

It is well known that the mean molecular mass is very nearly constant in the lower atmosphere, because turbulence overcomes the tendency for diffusive separation. As the altitude increases, the mean free path also increases, and so does the tendency toward diffusive separation. This tendency dominates above 100 km, so above this altitude each gas has its own vertical distribution with its own scale height. The lighter gases have larger scale heights, so the mean molecular mass continually decreases as the altitude increases above 100 km.(1) Although diffusive separation occurs, diffusive equilibrium does not necessarily exist, because the dissociation and recombination of oxygen are important processes between 70 and 200 km.(2)

At this point, the reader may well ask: "Why do we need a new method of determining the mean molecular mass? What is wrong with the old ones?" This question will be answered in the next section.

2. LIMITATIONS OF PRESENT MEASUREMENTS OF THE MEAN MOLECULAR MASS

The two main methods of determining the mean molecular mass, $\overline{m}$, are mass-spectrometric measurements(3-9) and extinction measurements(10). Uncertainties in the interpretation of mass-spectrometric measurements are related to the processes of calibration(11,12), recombination(13), and adsorption(14). Different mass spectrometers on the same rocket sometimes yield number densities differing by a factor of 2 or more.(15) The largest source of error in extinction measurements is uncertainty in the absorption cross sections, which may be as large as a factor of 2.(10) Errors in the measured concentrations of the individual constituents will be reflected in $\overline{m}$, which is computed from the equation

$$\overline{m} = \Sigma n_i m_i / (\Sigma n_i), \tag{1}$$

where n_i is the number density of the i-th constituent, and m_i is its molecular mass. The new method has been developed in order to reduce the error which is caused by the above sources.

3. THE NEW METHOD

The density scale height, H_ρ, is defined by the expression,

$$H_\rho \equiv -\rho/(\partial\rho/\partial Z), \tag{2}$$

where ρ is the density and Z is the altitude. It has been shown by Nicolet(1) that H_ρ can be closely approximated by the equation

$$H_\rho = H/(1+\beta), \tag{3}$$

where H is the pressure scale height, and β is its vertical gradient. The derivation of Equation (3) is given in the appendix. The relationship between H and $\overline{m}$ is contained in the expression

$$H = kT/(\overline{m}g), \tag{4}$$

in which k is Boltzmann's constant, T is the absolute temperature, and g is the local acceleration of gravity.(1) Equation (4) gives $\overline{m}$, the mass in grams of a single molecule. It is converted to the mass, $\overline{M}$, of a mole of molecules by

$$\overline{M} = 6.02 \times 10^{23}\ \overline{m}. \tag{5}$$

In the new method, H_ρ and β are measured by means of the orbital decay of conventional satellites(16) and the spin decay of paddlewheel satellites in highly eccentric orbits(17). These quantities are inserted in equation (3) to obtain H. Temperatures measured by several different methods (18-20) are used with H in equations (4) and (5) to deduce $\overline{M}$.

4. THE TEMPERATURE MEASUREMENTS

Many of the temperature measurements in references (18) to (20) were taken at sunspot minimum at an altitude of 225 km under nearly identical conditions of solar and corpuscular heating. These measurements are presented in Table 1. The relevant solar and corpuscular heating parameters used in model atmospheres are also tabulated. These parameters have been used with the Harris and Priester 1964 Model Atmosphere (reprinted in CIRA 1965) to adjust all the data to the conditions of Model 2 of CIRA 1965, which corresponds to average conditions at sunspot minimum. The adjustments were smaller than the standard deviation of the measurements. The column headings in Table 1 are: θ = local time, F = 10 cm flux, $\bar{F}$ = 5-month average solar flux, $\bar{a}_p$ = average geomagnetic planetary amplitude for the 12-hour period before the measurement, T_m = measured temperature, T_a = adjusted temperature. CIRA Model 2 corresponds to F = $\bar{F}$ = 75, and $\bar{a}_p$ = 2.

Table 1

Temperature Measurements at 225 km Near Sunspot Minimum

Observer	Date	θ	F	$\bar{F}$	$\bar{a}_p$	Tm	Ta
	D/M/Y	Hr/Min	10^{-22} $\frac{W}{m^2\ Hz}$		2γ	°K	
Authier[18]	11 April 64	1900	73	72	14	580 ± 40	549
"	13 April 64	0520	73	72	5	545 ± 40	548
Hall[19]	2 March 65	1709	76	74	12	750	736
"	3 March 65	0715	75	74	20	620	585
"	4 March 65	1711	75	74	5	750	766
Spencer[20]	28 Jan 64	2209	78	75	9	660	660
"	20 March 65	0042	74	75	4	680 ± 30	689
"	19 March 65	1309	76	75	5	775 ± 20	774

The adjusted temperatures are compared with Model 2 in Figure 1. Both the temperature at the altitude of measurement, T_{225}, and the temperature at the top of the atmosphere, T_∞, are shown. All the measurements at sunspot minimum are below the model, from 1 to 30%. Each method of measurement appears to give a different diurnal variation. Authier, et al.'s sodium glow cloud measurements appear not to give a diurnal variation, the mass-spectrometric measurements of Spencer, et al. seem to have a diurnal variation of about 100°K, and Hall and his colleagues' extinction measurements apparently yield a diurnal variation approaching 200°K. In addition, each method of measurement seems to be biased relative to the others. At least two of the three methods must be biased by approximately 50°K unless there is this much day-to-day variability in the atmosphere at middle latitudes. The apparent biases cannot be caused by an unmodeled seasonal or latitudinal variation, because all the measurements were made at latitudes between 31 and 38°N, and all but one were made in March and April. It would clearly be desirable to make all three types of measurement at one time and place.

Temperature measurements have also been made in the upper atmosphere by several other methods. Temperatures measured by the methods mentioned below have not been used in this paper, but they might be used with future measurements of H_ρ.

1. The spin modulation of mass-spectrometric data has apparently been used successfully in one case[21] to measure T. This method usually gives a large scatter in the measured temperatures.[22] Possible causes of this scatter include the ignoring of adsorption in the differential equation, the use of the hard-sphere model in the efflux term, and the complicated chamber geometry.

2. Incoherent scatter observations have been used at 18°N and 43°N to measure the complete diurnal variation of neutral temperature.[23] At 18°N, T measured by this method rises until sunset, but this effect might not be real, because the neutral temperature is not directly measured, and the theory is complicated. At 42°N the temperature measured by the same method falls considerably before sunset in summer.

3. Golomb, et al.[24] have used luminescent clouds of AlO to measure the temperature below 170 km. The measurements are in good agreement with other types of data.

4. A number of older ground-based methods of measurement have been reviewed by Mitra,[25] Bates[26] and Barbier[27]. It is sometimes difficult to determine the altitude to which these measurements apply, or whether the measured temperatures are the same as the kinetic temperature of the neutral atmosphere. Some of these uncertainties might be resolved by comparing the ground-based measurements with rocket measurements made at the same time and place. One should not reject these older methods without careful investigation, because, as Kallmann-Bijl[28] has pointed out, Martyn and Pulley[29] were able in 1936 to use these methods to infer the diurnal variations of upper-atmospheric temperature.

The temperature measurements listed in Table 1 were all made near sunspot minimum. It would be desirable to have some measurements near sunspot maximum so that M could be obtained for that period. Suitable data are rare, but two mass-spectrometric measurements above 200 km by Pokhunkov[29] in 1960 and 1961, and a sodium-cloud measurement by Blamont, et al.[30] at 270 km in 1960 have been used. The solar activity differed considerably during the three flights, so the measurements could not be checked against each other. The measurements are compared with the CIRA 1965 Model under the appropriate conditions of solar activity in Table 2. There are large disagreements which are not a smooth function of solar activity, suggesting large errors in some of the temperatures. Since these were the first measurements by these techniques at such high altitudes, this is not surprising.

Table 2

CIRA 1965 Model Temperatures vs. Measured Temperatures

Experimenter	Date	L.T.	Alt	Temperature (°K)	
	D/M/Y	hr/min	km	Meas.	CIRA
Blamont	10 Dec 1960	1746	370	1450 ± 75	1260
Pokhunkov	15 Nov 1961	1600	325-430	1470 ± 150	1079
"	"	"	200	1200 ± 120	914
"	23 Sept 1960	0056	200	895 ± 90	913
Average at sunspot minimum			225	663 ± 50	810

5. RESULTS

In order to compute the mean molecular mass by means of Equations (3) to (5), it is necessary to have measurements of scale height and temperature which apply to the same atmospheric conditions. Since the scale height measurements in references (16) and (17) were not made at the same times as the temperature measurements, the CIRA 1965 Model has been used to transform the scale height measurements to the conditions which prevailed when the temperatures were measured. Because the models imperfectly represent the atmosphere,[32] this transformation causes the error in the transformed scale heights to be larger than that of the scale height measurements. Comparisons have been made between the CIRA Model and the measurements of density scale height in reference (17), so they will not be repeated here. The relationships found in this reference have been used to make the transformation, which is a function of the altitude and the exospheric temperature, T_∞, of the CIRA Model.

The quantities which occur in the calculation of $\overline{M}$ from the measurements in Tables 1 and 2 are displayed in Table 3. The mean molecular masses from the sunspot minimum data and from Pokhunkov's 1960 measurement appear reasonable, and are within one standard deviation of the CIRA values. Pokhunkov's 1961 measurement yields an impossible result, and Blamont's 1960 measurement leads to a highly unlikely value of $\overline{M}$. Without intending to, we have discovered a method of testing the plausibility of atmospheric temperature measurements.

Table 3

Calculation of $\overline{M}$

EXPERIMENTER	BLAMONT	POKHUNKOV			AVERAGE SS. MIN
Date	Dec. 10, 1960	Nov. 15, 1961		Sept. 23, 1960	1964-65
Altitude (km)	370	370	200	200	225
T (°K)	1450 ± 75	1470 ± 150	1200 ± 120	895 ± 90	663 ± 50
CIRA T_∞ (°K)	1260	1079	1079	1042	898
H_ρ (km)	53 ± 3	50 ± 3	27 ± 2	27 ± 2	30 ± 2
β	0.10 ± .02	0.10 ± .02	0.14 ± .02	0.14 ± .02	0.14 ± .02
H (km)	58 ± 3	55 ± 3	31 ± 2	31 ± 2	34 ± 2
g (cm/sec^2)	872	872	920	920	910
$\overline{M}$ (gm/mole)	24 ± 3	26 ± 3	35 ± 4	26 ± 3	18 ± 2
CIRA $\overline{M}$ (gm/mole)	18	17	23-	23	20.5
CIRA H (km)	67	59	37-	36	36

6. ERROR DISCUSSION

It is a consequence of Equations (3) to (5) and the independence of the methods of measurement of the parameters that the fractional error in $\overline{M}$ is given very nearly by

$$\Delta\overline{M}/\overline{M} = [(\Delta H_\rho/H_\rho)^2 + (\Delta T/T)^2]^{1/2} \quad (6)$$

The error in H_ρ consists in the error of measurement, the error in transforming H_ρ to the solar heating conditions corresponding to the temperature measurements, and the error caused by a possible variation in the drag coefficient. The gradient of the scale height contributes a negligible error to the computed $\overline{M}$.

The fractional error caused by measuring and transforming H_ρ is estimated to be 0.07 in the present case. The error caused by ignoring possible variations in C_d has been estimated by assuming that the angular distribution of the re-emitted molecules was that found by Alcalay and Knuth at 1 e.v. for an old glass surface, and that the C_d varied from the value found for Ariel 2 to that for Explorer 6.[33] These assumptions yield a fractional error of 0.04 caused by the possible variation in drag coefficient.

Only in the case of the average temperature measurement at sunspot minimum was it possible to make an error estimate which was independent of the experimenter's estimate. The fractional error in the average temperature at sunspot minimum was 0.08. In the other cases, the error assigned by the experimenter was adopted. If the derived $\overline{M}$ seemed unreasonable, this was taken to mean that the error in temperature had been under-estimated by the experimenter.

7. CONCLUSIONS

Although the earliest temperature measurements made above 200 km by rockets appear in some cases to have been in error by 20 to 40%, the discrepancies among temperature measurements had been reduced to the range of 10 to 20% by the time of sunspot minimum. By taking the average of measurements by several methods under similar conditions of solar activity, it was possible to reduce the error in temperature measurements below 10%. The different methods of measurement still have biases and diurnal variations which differ by the order of 10%, but it is hoped that these will be further improved in the future.

It has been possible in the present calculations to verify the average value of $\overline{M}$ in the CIRA Model at sunspot minimum with an accuracy of approximately 11%. It has not been possible to improve on the Model because of errors in temperature measurements and uncertainties in using the model to transform scale height measurements from one condition of solar activity to another. However, it is hoped that these difficulties can be overcome in the Marshall Space Flight Center's Project ODYSSEY, in which it is proposed to measure the temperature by several different methods, the density scale height, and the drag coefficient simultaneously.

APPENDIX. THE DERIVATION OF NICOLET'S EQUATION

The pressure scale height, H, can be defined by the expression

$$H \equiv -p/(\partial p/\partial z),$$

where p is pressure and z is altitude. Over altitude ranges of 20 or 30 km, the variation of H with z can be very closely approximated by the linear expression

$$H = H_o + \beta(Z-Z_o),$$

where β is the vertical gradient of H. On the other hand, we have from the hydrostatic approximation

$$\partial p/\partial z = -\rho g = -p/H,$$

where ρ is the density and g the local acceleration of gravity.

We can use the linear variation of H to write

$$\rho = \frac{p}{gH} = \frac{p}{g[H_o + \beta(Z-Z_o)]} \; .$$

By simple differentiation,

$$\frac{\partial\rho}{\partial Z} = \frac{\partial p}{\partial Z}\left(\frac{1}{gH}\right) - \frac{p}{gH^2}\beta = -\frac{p}{gH^2}(1+\beta)$$

We are seeking an expression for the density scale height, H_ρ, which is defined by the expression

$$H_\rho \equiv -\rho/(\partial\rho/\partial Z).$$

Substituting from the above expressions,

$$H_\rho = \frac{-(p/gH)}{-(p/gH^2)(1+\beta)}$$

$$H_\rho = \frac{H}{1+\beta}$$

The only assumptions contained in the above derivation are the hydrostatic law, the ideal gas law, and a linear dependence of H on Z in a local region. These assumptions should be very nearly true at altitudes of 200 to 400 km.

REFERENCES

1. Nicolet, M. in J. A. Ratcliffe (Ed.), 1960: Physics of the Upper Atmosphere. N. Y. and London, Academic Press, 17-72.

2. Shimazaki, T., 1967: Dynamic effects on atomic and molecular oxygen density distributions. J. Atmosph. Terr. Phys., 29, 723-747.

3. Meadows, E. B. and J. W. Townsend, Jr., IGY rocket measurements, in H. Kallmann-Bijl (Ed.), 1960: Space Research. Amsterdam, North-Holland Publ. Co., 175-198.

4. Nier, A. O., J. H. Hoffman, C. Y. Johnson, and J. C. Holmes, 1964: Neutral composition of the atmosphere. J. Geophys. Res., 69, 979-989.

5. Nier, A. O., J. H. Hoffman, C. Y. Johnson, and J. C. Holmes, 1964: Neutral constituents of the upper atmosphere. J. Geophys. Res., 69, 4629-4636.

6. Schaefer, E. J. and M. H. Nichols, 1964: Upper air neutral composition measurements. J. Geophys. Res., 69, 4649-4660.

7. Reber, C. A. and M. Nicolet, 1965: Investigation of the major constituents. Planet. Space Sci., 13, 617-646.

8. Mauersberger, K., D. Müller, D. Offermann, and U. Von Zahn, Neutral constituents of the upper atmosphere, in R. L. Smith-Rose (Ed.), 1967: Space Research VII, 1150-1158.

9. Taeusch, D. R., R. Smith, H. B. Niemann, G. R. Carignan, and J. O. Ballance: MUMP diurnal survey of the thermosphere, I, paper presented at COSPAR meeting in London, July 1967.

10. Hall, L. A., W. Schweizer, and H. E. Hinteregger, 1965: Improved extreme ultraviolet absorption measurements, J. Geophys. Res., 70, 105-111.

11. Friedman, M. P., 1966: A critical survey of upper atmosphere density measurements. Smithsonian Astrophys. Obs. Sp. Rept. No. 217.

12. Cook, G., 1967: Comparison of air densities from orbital decay and instruments. Phil. Trans. Roy. Soc. (London), A, 262, 172-184.

13. Von Zahn, U., 1967: Mass spectrometric measurements of atomic oxygen. J. Geophys. Res., 72, 5933-5938.

14. Moe, K. and M. M. Moe, 1967: The effect of adsorption on densities measured by orbiting pressure gauges, Planet. Space Sci., 15, 1329-1332.

15. Hedin, A. E. and A. O. Nier, 1966: A determination of the neutral composition. J. Geophys. Res., 71, 4121.

16. King-Hele, D. G. and J. M. Rees, 1962: Scale height in the upper atmosphere, derived from changes in satellite orbits. Proc. Roy. Soc. (London), A, 270, 562-587.

17. Moe, K., D. Klein, G. Maled, and L. Tsang: Density scale heights at sunspot maximum and minimum from satellite data. (To be published in Planet. Space Sci. about April 1968.)

18. Authier, B., J. E. Blamont, and M. L. Lory-Chanin, 1966: Altitude comparison of electron and neutral gas temperatures. Space Research VI, Amsterdam, North-Holland Publ. Co., 383-385.

19. Hall, L. A., C. W. Chagnon, and H. E. Hinteregger, 1967: Daytime variations in the composition of the upper atmosphere. J. Geophys. Res., 72, 3425-3427.

20. Spencer, N. W., D. R. Taeusch, and G. R. Carignan, 1966: N_2 temperature and density data. Ann. de Géophys., 22, 151-160.

21. Hedin, A. E., C. P. Avery, and C. D. Tschetter, 1964: An analysis of spin-modulation effects on data obtained with a rocket-borne mass spectrometer. J. Geophys. Res., 69, 4637-4648.

22. Harris, I., and N. W. Spencer, in W. H. Hess (Ed.), 1965: Introduction to Space Science. New York, Gordon and Breach, 112.

23. Nisbet, J. S., 1967: Neutral atmospheric temperatures from incoherent scatter observations. J. Atmos. Sci., 24, 586-593.

24. Golomb, D., O. Harang, and F. P. Del Greco, 1967: Upper atmosphere densities and temperatures, J. Geophys. Res., 72, 2365-2370.

25. Mitra, S. K., 1948: The Upper Atmosphere. Calcutta, Royal Asiatic Soc. Bengal, 507-519.

26. Bates, D. R., in J. A. Ratcliffe (Ed.), 1960: Physics of the Upper Atmosphere, N. Y. and London, Academic Press, 226-228 and 339-343.

27. Barbier, D., Introduction a l'étude de la luminescence atmosphèrique, in C. De Witt, J. Hieblot, and A. Lebeau (Eds.), 1963: Geophysics The Earth's Environment. N. Y. and London, Gordon and Breach, 303-372.

28. Kallmann-Bijl, H. K. and W. L. Sibley, Diurnal variation of temperature, in P. Muller (Ed.), 1962: Space Research IV, Amsterdam, North-Holland Publ. Co., 279-301.

29. Martyn, D. F. and O. O. Pulley, 1936: The temperatures and constituents of the upper atmosphere. Proc. Roy. Soc. (London) 154A, 455-486.

30. Pokhunkov, A. A., Gravitational Separation, in W. Priester (Ed.), 1963: Space Research III, Amsterdam, North Holland Publ. Co., 132-142.

31. Blamont, J. E., M. L. Lory, J. P. Schneider, and G. Courtes, Mesure de la température de la haute atmosphère, in H. C. Van de Hulst, C. de Jager and A. F. Moore (Eds.), 1962: Space Research II, Amsterdam, North-Holland Publ. Co., 974-980.

32. Moe, K., 1967: The corpuscular heating effect. Planet. Space Sci., 15, 1821-1827.

33. Moe, K.: Recent experimental evidence bearing on satellite drag coefficients. (To be published in the AIAA J. about June 1968,)

FIG 1 COMPARISON OF CIRA MODEL 2 WITH ADJUSTED TEMPERATURE MEASUREMENTS