JSC-08683

NASA TECHNICAL MEMORANDUM

NASA TM X-58114 March 1974



# A THERMODYNAMIC CHART FOR THE MARS ATMOSPHERE

¥74-20525

(NASA-TN-X-58114) A THEPMODYNAMIC CHAFT FOR THE MAFS ATMOSPHERE (NASA) 20 D HC S4.00 G3/30 34505



NATIONAL ARRONAUTICS AND SPACE ADMINISTRATION

LYNDON B. JOHNSON SPACE CENTER

HOUSTON, TEXAS 77058

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7 Authorisi		8 Performing Organization Report No
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David E. Pius, JSC		JSC-08683
		10 Work Unit No
9 Performing Organization Name and Address	6	951-16-00-00-72
Lyndon B. Johnson Space Center		T1 Contract or Grant No
Houston, Texas 77058		
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12 Supersonal Association and Address	·····	
It. Shoredaring regardy reame and reduces		Technical Memorandum
National Aeronautics and Space Administration		14 Sponsoring Agency Code
Washington, D.C. 20546		
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15. Supplementary Notes		
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## A THERMODYNAMIC CHART FOR THE MARS ATMOSPHERE

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#### A THERMODYNAMIC CHART FOR THE MARS ATMOSPHERE

#### By David E. Pitts Lyndon B. Johnson Space Center

#### SUMMARY

A thermodynamic chart known as a tephigram (temperature/entropy gram) was drawn for the Mars atmosphere by using an X-Y plotter and a computer. The tephigram has temperature as the abscissa and the  $\log_{10}$  of potential temperature as the ordinate. Lines of pressure, temperature, potential temperature, saturation-

mixing ratio, and equivalent potential temperature are presented so that watervapor-condensation processes may be studied for a range of temperatures from 80 to 320 K, for a range of potential temperatures from 100 to 390 K, and for a range of pressures from 0.1 to 8 millibars.

The region in which carbon dioxide condensation can occur is shown at temperatures of 150 K or less and is represented by an area on the chart. A minimum of assumptions was made so that maximum use could be made of the chart. These assumptions, that the surface pressure is 3 millibars and the atmosphere is 100 percent carbon dioxide, are consistent with analyses of the Mariner IV

data. Trace amounts of water vapor (approximately  $1 \times 10^{-3}$  centimeter precipitable) were assumed.

#### INTRODUCTION

The fact that so many disciplines are involved in the interpretation of phenomena in the Mars atmosphere increases the difficulty of coordinating a self-consistent analysis of the state of the atmosphere. Thus, the purpose of this report is to present a meteorological chart for the atmosphere of Mars that will aid investigators in the interpretation of in situ measurements (e.g., Viking), remote measurements from orbiters or from flyby missions, astronomical observations, and meteorological theories.

### SYMEOLS

$$c = \frac{m_d}{n_w}$$

$$c_{pd} = \frac{m_d}{m_{v}}$$

$$c_{pd} = \frac{m_d}{m_{v}}$$

$$c_{1} = \frac{m_d}{m_{v}}$$

$$f_{w} =$$

 $P_2$  some pressure higher than  $P_1$ , millibars

 $Q = 8(1/T)^{-1/K}$ 

- R<sub>d</sub> universal gas constant, 1.98583 calories/mole-kelvin
- r mixing ratio, grams/kilogram
- $\bar{r}$  average mixing ratio from  $P_{o}$  to  $P_{z}$ , grams/kilogram
- r saturation-mixing ratio, grams/kilogram
- T temperature, kelvin
- $\bar{T}$  average temperature between  $P_1$  and  $P_2$ , kelvin
- T<sub>d</sub> dewpoint temperature, kelvin
- $\alpha$  specific volume  $\frac{1}{\rho}$ , centimeters<sup>3</sup>/gram
- $\beta$  constant from reference 9 used in equation (30)
- $\Delta Z$  geopotential altitude between  $P_1$  and  $P_2$ , meters
- $\eta$  constant from reference 9 used in equation (30)
- θ potential temperature based on surface pressure of 8 millibars and an atmosphere of approximately 100 percent carbon dioxide, kelvin
- $\theta_E$  equivalent potential temperature based on a change of phase of water in a 100-percent-carbon-dioxide atmosphere, kelvin
- $\xi$  constant from reference 9 used in equation (30)
- ρ atmospheric gas density, grams/centimeter<sup>3</sup>
- entropy per unit mass

#### CONSTRUCTION OF THE MARS TEPHIGRAM

Saucier and Elliott (ref. 1) developed a thermodynamic chart or tephigram for the Earth atmosphere that has proved extremely useful. A tephigram for the Mars atmosphere has been developed that will aid investigators in interpreting the maximum amounts of water vapor from the range of surface temperatures observed by the Mariner IX infrared radiometer (ref. 2) of 195 K (morning terminator) to 250 K (local noon) and in interpreting temperature structure deduced from S-band occultations (ref. 3) and from temperature sounders like the infrared interferometer spectrometer (ref. 4) or from entry probes such as the Viking lander. A copy of the Mars tephigram is included at the end of this report.

Most of the major features of the tephigram are common to other thermodynamic charts; however, the tephigram was chosen because the right angle between the isotherms (temperature T) and dry adiabats (potential temperature  $\theta$  lines) makes it easier to detect variations in the temperature lapse rate. Area is also proportional to energy, as is true of any true thermodynamic chart.

Assumptions consistent with Mariner IV and Mariner 1V data were used (i.e., a surface pressure of 8 millibars and a l00-percent-carbon-dioxide  $(CO_2)$  atmosphere, with trace amounts of water  $(H_2O)$ ). A. J. Kliore et al. (ref. 3) found a range of surface pressures between 2.9 and 8.3 millibars and elevation differences as great as 13 kilometers from Mariner IX occultations at S-band frequencies. Recent models have used 50 to 100 percent  $CO_2$  corresponding to surface pressures of 15 and 5 millibars, respectively (ref. 5). However, with lower surface pressures being corroborated more recently, there is increasing use of

surface pressures being corroborated more recently, there is increasing use of 100 percent CO<sub>2</sub> (ref. 4) primarily because no other gas has been detected in large quantities (ref. 5).

Lines of pressure, temperature, potential temperature, saturation-mixing ratio, and equivalent potential temperature are presented so that water-vaporcondensation processes may be studied for a range of pressures from 0.1 to 8 millibars, for a range of temperatures from 80 to 320 K, for a range of potential temperatures from 100 to 390 K, for a range of equivalent potential temperatures from 200 to 400 K, and for a range of saturation-mixing ratios

 $r_s$  (0/00; i.e., grams per kilogram) from 10<sup>-9</sup> 0/00 to 10<sup>5</sup> 0/00.

A line representing the equivalence of the saturation vapor pressure of  $CC_2$  and total pressure is drawn on the tephigram to indicate the area where  $CO_2$  condensation can occur. A temperature of 150 K or less is necessary at the surface; at 0.2 millibar, 126 K or less is required. This temperature is a necessary but not sufficient condition for condensation because small droplets require higher vapor pressure for equilibrium than does the flat surface assumed in the vapor pressure equations. Because  $CO_2$  is the major constituent of the atmosphere, condensation of  $CO_2$  will not effectively change the amount of  $CO_2$  (i.e., mixing ratio); however, it will tend to stabilize the temperature at the freezing point of  $CO_2$  and cause a reduction in surface pressure.

Using a computer program, approximately 20 000 data points were generated for the tephigram. These data were processed by an X-Y plotter that draws lines to an accuracy of five significant decimal digits. The variability with temperature of specific heat at constant pressure and the latent heat of vaporization should be accounted for with such accurate plotting and computer capability; this was accomplished with second-order curve fits on temperature. All quantities were plotted relative to the ordinate  $\log_{10} \theta$  and abscissa T; that is, no lines were plotted relative to the pressure lines or the saturation-mixingratio lines.

#### GRID STRUCTURE

Isotherms are the vertical yellow lines entered for each 1 K; the heavy lines are for each 10 K in temperature. The isotherms are labeled at the lower ends.

Dry adiabats or isopleths of potential temperature and of entropy are the horizontal yellow lines that are drawn in the same scheme as the isotherms and labeled in kelvin. The vertical scale is  $\log_{10} \theta$ , which is directly proportional to  $\log_{e} \theta$  where  $\theta$  is potential temperature in kelvin. Thus, because specific entropy (entropy per unit mass)

$$\Phi = C_{pd} \log_e \theta + C_1 \tag{1}$$

where  $C_{pd}$  is specific heat at constant pressure for  $CO_2$  gas and  $C_1$  is a constant, and because the horizontal scale is proportional to temperature, the chart is a temperature/entropy diagram or tephigram.

Area on the tephigram (ref. 1) shows that one form of the first law of thermodynamics is

$$dq = \frac{C_{pd}}{m} dT - \alpha dP$$
 (2)

where dq is change of heat in a unit mass of gas, m is molecular weight of ambient atmosphere, P is pressure, and  $\alpha$  is specific volume  $1/\rho$ . B cause

$$\alpha = \frac{R_{d}T}{Pm}$$
(3)

where  $R_d$  is the universal gas constant, equation (2) may be rewritten as

$$\frac{dq}{T} = \frac{C_{pd}}{m} d(\ln T) - \frac{R_d}{m} d(\ln P)$$
(4)

Both terms on the right-hand side of this equation are exact differentials, so

$$\int \frac{\mathrm{d}q}{\mathrm{T}} = \int \mathrm{d}\Phi = 0 \tag{5}$$

Potential temperature is defined as the temperature corresponding to the surface pressure  $P_0$ . By the integration of equation (4), from  $P_0$  to P (0 to T), using equation (5), one obtains

$$\theta = T \left(\frac{P_{o}}{P}\right)^{\frac{R_{d}}{C_{pd}}}$$
(6)

where  $P_0 \approx 8$  millibars for Mars. Then

$$\ln \theta = \ln T + \frac{R_d}{C_{pd}} \ln P_o - \frac{R_d}{C_{pd}} \ln P$$
(7)

Taking the differential gives

$$d(\ln \theta) = d(\ln T) - \frac{R_d}{C_{pd}} d(\ln P)$$
(8)

Substituting equation (8) into equation (4) gives

$$\frac{dq}{T} = C_{pd} d(\ln \theta)$$
(9)

Thus, the work done dq in a cyclic process is

$$\int dq = C_{pd} \int T d(\ln \theta)$$
 (10)

Therefore, because T is the abscissa and log  $\theta$  is the line. area on the tephigram represents energy.

Isobars are the green curves sloping upward to the right, labeled in millibars, and drawn in 0.1-millibar increments from 8 millibars to 7 millibar and in 0.01-millibar increments from 1 millibar to 0.1 millibar. They were calculated by using the following equations. Equation (6) in log form is

$$\ln \theta = \ln T + \frac{R_d}{C_{pd}} \ln\left(\frac{8}{P}\right)$$
(11)

SO

$$\log_{10} \theta = 0.43429448 \left[ \ln T + \frac{R_{d}}{C_{pd}} \ln \left(\frac{8}{P}\right) \right]$$
(12)

Isopleths of saturation-mixing ratio  $r_s$  are the green lines that slope upward to the left and are not greatly curved. Saucier and Elliott (ref. 1) define  $r_s$  as

$$r_{s} = \frac{m_{w} f_{w} e_{sw}}{m_{d} \left(P - f_{w} e_{sw}\right)}$$
(13)

where  $m_W$  is the molecular weight of water vapor,  $f_W$  is a factor to account for nonideology of gas,  $e_{_{\rm EW}}$  is the saturation vapor pressure for water, and  $m_d$  is the molecular weight of CO<sub>2</sub> gas. For the low pressures involved here,  $f_w = 1$  may be assumed and still be accurate within ±0.02 percent (ref. 6). Thus, equation (13) may be simplified to

$$\mathbf{r}_{s} = \frac{\mathbf{m}_{w}}{\mathbf{m}_{d}} \frac{\mathbf{e}_{sw}}{\mathbf{P} - \mathbf{e}_{sw}}$$
(14)

However, for plotting purposes,  $r_s$  had to be a function of T and  $\log_{10} \theta$ . Equation (6) may be solved for P

$$P = 8 \left(\frac{T}{\theta}\right)^{\frac{C_{pd}}{R_{d}}}$$
(15)

and then substituted into equation (14) giving

$$\mathbf{r}_{g} = \frac{\frac{\mathbf{m}_{g} \mathbf{e}_{gw}}{C}}{\frac{\mathbf{p}_{d}}{\mathbf{R}_{d}}}$$
(16)

Solving for  $\theta$  gives

$$\theta = T \left[ \frac{m_d r_s \theta}{\left( m_w + m_d r_s \right) e_{sw}} \right]^{\frac{R_d}{C_{pd}}}$$
(17)

or

$$\log_{10} \theta = 0.43429448 \left| \ln T + \frac{R_{d}}{C_{pd}} \ln \left[ \frac{m_{d} r_{g} \theta}{(m_{w} + m_{d} r_{g}) e_{gw}} \right] \right|$$
(18)

The saturation vapor pressure  $e_{sw}$  that was used in equations (16) to (18) was taken from Saucier (ref. 7). For water

$$e_{sw} = 6.11 \times 10^{[7.5T/(237.3+T)]}$$
(19)

For ice

$$e_{si} = 6.11 \times 10^{[9.5T/(265.0+T)]}$$
 (20)

where e is saturation vapor pressure for water ice and T i in degrees celsius.

Isopleths of equivalent potential temperature, which are approximate pseudoadiabats, are the curved green lines that are concave toward low temperature and potential temperature and are entered for each 10 K from 200 to 400 K. The values of equivalent potential temperature  $\theta_E$  are found by following the pseudoadiabat to the left border of the chart and reading the value in the potential temperature scale; that is,  $\theta_E$  approaches  $\theta$  at low temperature. The  $\theta_E$  lines were drawn by using the expansion of the Rossby equation (ref. 1)

$$\theta_{\rm E} = \theta \left( 1 + \frac{m_{\rm d}}{m_{\rm w}} r_{\rm s} \right)^{\rm R} \exp \left( \frac{L_{\rm w} r_{\rm s}}{C_{\rm pd}} \right)$$
(21)

where L is the latent heat of vaporization for water, and solving for  $\theta = f(T)$ . Since  $r_g = f(\theta,T)$  in equation (16),  $\theta$  must be found by taking successive approximations of  $\theta$  in the form

$$\mathbf{f}(\theta) = \theta \left( \mathbf{l} + \frac{\mathbf{m}_{d}}{\mathbf{m}_{w}} \mathbf{r}_{s} \right)^{\frac{R_{d}}{C_{pd}}} \exp \left( \frac{\mathbf{L} \cdot \mathbf{r}_{s}}{C_{pd}} \right) - \theta_{E}$$
(22)

until  $f(\theta) = 0$ . Successive approximations are found by Newton's method (ref. 8).

$$\theta_{n+1} = \theta_n - \frac{f(\theta_n)}{f'(\theta_n)}$$
(23)

for a approximations. Five such approximations were sufficient for each data point when solutions for the  $\theta_{\rm E}$  line were started at low temperature and worked to higher temperature 1 K at a time. The preceding solution is used each time as the first guess to the next point.

Taking the derivative of equation (23) with respect to  $\theta$  gives

$$\mathbf{f}^{*}(\theta) = \left(1 + Cr_{s}\right)^{K} \exp \left(\frac{L_{v}r_{s}}{C_{pd}T}\right) \left(1 + \theta \frac{dr_{z}}{d\theta} \left[CK\left(1 + Cr_{s}\right)^{-1}\right] + \frac{L_{v}}{C_{pd}T}\right)$$
(24)

where

$$C = \frac{\mathbf{a}}{\mathbf{a}}_{\mathbf{v}}$$
(25)

$$K = \frac{R_{d}}{C_{pd}}$$
(26)

The derivative of  $r_s$  with respect to  $\theta$  in equation (16) is

$$\frac{\mathrm{d}\mathbf{r}_{s}}{\mathrm{d}\theta} = \frac{-\mathrm{Ce}_{sw} Q\left(-\frac{1}{K}\right) \theta^{-\left(\frac{1}{K}+1\right)}}{\left(Q\theta^{-\frac{1}{K}} - e_{sw}\right)^{2}}$$
(27)

where

$$Q = 8\left(\frac{1}{T}\right)^{-\frac{1}{K}}$$
(28)

During the calculations of the P,  $r_s$ , and  $\theta_E$  lines,  $C_{pi}$  was assumed to vary with temperature according to the formula

$$C_{pd} = 6.6367 + 1.396 \times 10^{-3} T + 2.0415 \times 10^{-5} T^2$$
 (29)

which was obtained by performing a curve fit of the form

$$C_{pd} = \eta + \beta T + \xi T^2$$
 (30)

on data from McBride et al. (ref. 9), where n,  $\beta$ , and  $\xi$  are constants. The value of L was assumed to vary in a manner similar to that in equation (30). In this case, the curve fit was performed using data from List (ref. 6).

$$L_{u} = 816.9432937 - 1.005091237T + 0.0007^{2}6001T^{2}$$
(31)

Performance of the thickness evaluation was similar to that done by Saucier and Elliott (ref. 1) with modifications for the Mars atmosphere.

$$\Delta Z = 50.3777\overline{T} \log_{e} \left(\frac{P_{1}}{P_{2}}\right)$$
(32)

where the depth of the layer  $\Delta Z$  in geopotential meters is proportional to the log<sub>e</sub> of the pressures at the lower  $P_1$  and upper  $P_2$  boundaries and the mean temperature of the layer  $\bar{T}$ .

The carbon dioxide equilibrium saturation line is the very heavy line on the left-hand side of the chart. It was drawn by assuming that the pressure of the atmosphere (160 percent  $CO_2$ ) was equal to the saturation vapor pressure for  $CO_2$  (ref. 10).

$$P = 1.333225685 \times 10 \left( \frac{-1367.344845}{T} + 9.9082 \right)$$
(33)

where T is in d grees Celsius. The region to the left of this line represents the saturation r gion for a plane surface of solid CO<sub>2</sub>. This statement, of

course, does not mean that saturation must occur in this region. For example, when small particles of  $CO_2$  are involved, saturation will not occur until a lower temperature is reached. When  $CO_2$  sublimes, 137.037 cal/g are involved (ref. 11).

#### GRAPHICAL OPERATIONS

The processes briefly described in the following sections are some of the more common operations performed with the tephigram. A more detailed treatment can be found in reference 7.

#### Adiabatic Processes

Air heated near the surface ascends adiabatically ( $\theta$  is conserved); that is, the pressure and temperature can be found by following the  $\theta$  line corresponding to the original pressure and temperature. If the surface pressure is 8 millibars and the surface (air) temperature is 230 K, rising air stays at a constant  $\theta = \geq 30$  K. Thus, when the pressure is 4.5 millibars, the temperature is 197 K.

#### Saturation

The amount of water necessary for condensation at any pressure and temperature is given by the corresponding  $r_s$  as read from the chart. For example, for a pressure of 4.5 millibars and a temperature of 197 K, the saturationmixing ratio  $r_s$  is 0.1 0/00. If the mixing ratio  $r = r_s$ , saturation occurs and the parcel no longer ascends adiabatically. Instead, the parcel follows a  $\theta_E$  line corresponding to the pressure and temperature where  $r = r_s$  (the base of the cloud). If the surface pressure is 8 millibars, the surface temperature is 230 K, and the mixing ratio is 0.1 0/00, the parcel is lifted adiabatically and conserves moisture r at 4.5 millibars pressure and 197 K. Above this altitude, pressure and temperature values can be read from the  $\theta_E$  line of 232 K because the processes are such that  $\theta_E$  is conserved.

#### Isobaric Processes

Isobaric cooling from the original pressure and temperature with P remaining constant without addition or removal of moisture (r is constant) results in saturation when  $r = r_s$ . This process defines the dewpoint temperature  $T_d$ . Isobaric cooling results in stability or inversion and will produce fog if the moisture content r is sufficiently high. If the surface pressure is 8 millibars, the surface temperature is 230 K, and the water vapor is 0.1 0/00; then the dewpoint temperature  $T_d$  is 202 K. Isobaric warming near the surface

causes instability. This condition produces vertical motion and is commonly thought to produce clouds on Mars.

#### Stability

Unsaturated air is stable or unstable according to the relationship of the temperature lapse rate to that of the  $\theta$  lines:  $\frac{\partial \theta}{\partial P} = 0$  is neutral,  $\frac{\partial \theta}{\partial P} < 0$  is stable, and  $\frac{\partial \theta}{\partial P} > 0$  is unstable. Saturated air is stable or unstable according to the relationship of the temperature lapse rate to that of the  $\theta_E$  lines. Thus, it is possible that an air column could be stable for unsaturation and unstable upon saturation. This particular situation is called conditional instability. Thus, above saturation, the parcel of air would be in free convection (at the '-vel of free convection):  $\frac{\partial \theta}{\partial P} = \frac{\partial \theta}{\partial P}$  is neutral,  $\frac{\partial \theta}{\partial P} < \frac{\partial \theta}{\partial P}$  is unstable.

#### Effects of Diurnal Heating

As morning comes, the nighttime inversion is removed and the ground temperature becomes progressively higher as heating continues. The air column is modified to an adiabatic state in the lower regions while the higher regions remain undisturbed. The area between the final adiabatic lapse rate, the surface pressure curve, and the original sounding represents the energy added by insulation. If the heating from below is intense enough, condensation may occur. The point at which condensation occurs is the convective condensation level.

#### Nighttime Fog Due to Inversions

When rapid cooling near the surface occurs,  $\cdot$  mixing ratio may be reached by the saturation-mixing ratio in the resulting pressure temperature sounding. This condition results in nighttime fog.

#### Columnar Mass of Water

The amount of  $H_0^0$  in a column (grams per square centimeter) is equal to

$$M = 1000 \int_{0}^{z} r(0/00) \rho(z) dz \qquad (34)$$

where M is the columnar mass of  $H_2^0$ ,  $\rho$  is the atmospheric gas density, and r is in grams per kilogram. However, if the average mixing ratio  $\bar{r}$  from the surface pressure  $P_{0}$  to the pressure  $P_{z}$  at altitude z is substituted for r, then

$$M = \bar{r} \int_0^z \rho(z) dz = \bar{r} \frac{P_0 - P_z}{G}$$
(35)

where G is the acceleration of gravity for Mars. To find the amount of precipitable  $H_2^0$  in centimeters, divide by the density of water ( $l g/cm^3$ ).

#### CONCLUDING REMARKS

The tephigram of the Mars atmosphere presents a means of performing detailed graphical operations such as adiabatic processes, saturation, isobaric processes (such as radiative cooling), stability changes with condensation, and other processes without the aid of costly computer analysis. Thus, analyses of the Mars atmosphere may be facilitated by the Mars tephigram as studies of the Earth atmosphere have been by the tephigram of Saucier and Elliott.

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FOLDOUT FRAME - 1

