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Technical Notes

Thermodynamic Properties of the Low Martian Atmosphere

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Nomenclature

c_v = specific heat at constant volume, kJ/kg-K
h = enthalpy, kJ/kg, kJ/kg$_{CO_2}$
M = molecular weight, kg/kmol
m = mass, kg
P = pressure, kPa
P_c = critical-point pressure, kPa
P_s = saturation pressure, kPa
P_{tp} = triple-point pressure, kPa
R = gas constant, $\bar{R}/M$, kJ/kg-K
$\bar{R}$ = universal gas constant, 8.3144 kJ/kmol-K
s = entropy, kJ/kg-K, kJ/kg$_{CO_2}$-K
T = temperature, K
T_c = critical-point temperature, K
T_s = saturation temperature, K
T_{tp} = triple-point temperature, K
u = internal energy, kJ/kg
v = specific volume, m^3/kg, m^3/kg$_{CO_2}$
W = mass ratio, kg$_{N_2}$/kg$_{CO_2}$
X_i = mass fraction, kg$_i$/kg
Y_i = mole fraction, kmol$_i$/kmol
Z = compressibility factor
ρ = density, kg/m^3

Subscripts

CO_2 = carbon dioxide
i = gas i
N_2 = nitrogen

I. Introduction

CURRENTLY, Mars is the target of NASA's most intensive scientific exploration of another planetary body since the Apollo Program. Much of this activity will involve exploring the surface of Mars and the search for extraterrestrial life, which will require an accurate knowledge of the thermodynamic properties of the Mars atmosphere.

The objective of this Note is to develop data for the thermodynamic properties of Mars atmosphere at, or near, the surface, where freezing and thawing of the CO_2 can occur. These data must be known to develop missions that explore the surface and lower atmosphere of Mars.

Thermodynamic and transport properties of the Martian atmospheric gases have been developed for atmospheric entry conditions.[1–4] The bulk of the data is at the high temperatures and pressures that occur behind shock waves of spacecraft during atmospheric entry and not at the low pressures and temperatures at the Martian surface.

The composition and structure of the Mars atmosphere as observed from the Mariner spacecraft flybys has been critically reviewed by Hunten.[5] Mars has a thin atmosphere, free of extensive cloudiness and transparent to most of the sun's radiation. Thus, most of the solar heat is deposited at the surface.

The atmosphere of Mars is approximately 95.5% carbon dioxide (CO_2) with the remainder made up mainly of nitrogen (N_2), argon (Ar), and smaller amounts of carbon monoxide (CO) and oxygen (O_2). Average data for Mars atmosphere (COSPAR Northern hemisphere mean reference data) are given by Pitts et al.[6] The composition of the atmosphere is assumed to be constant with altitude and is fairly well modeled as 95% CO_2 and 5% N_2 by mole fraction.[2–4,6,7]

At the same altitude the Mars temperature and pressure are considerably lower than that of Earth.[6,7] At the Mars surface the average temperature, pressure, and density are 214 K, 0.6266 kPa, and 0.0155 kg/m^3, respectively. Because of solar radiation, the surface temperature can vary by as much as ±25 K from its average value during the Mars day.[8] The surface pressure (measured by the two Viking landers) varies seasonally, ranging from about 0.5 to 1 kPa.

II. Analysis

A. Equation of State

The Mars atmosphere is assumed to have a composition of 95% CO_2 and 5% N_2 by volume. In this analysis, the atmosphere is treated as a nonreacting mixture of real gases. The equation of state is

$$P = Z \rho \bar{R} T / M \tag{1}$$

where $M = Y_{CO_2} M_{CO_2} + Y_{N_2} M_{N_2}$. The compressibility factor Z for both CO_2 and N_2 is evaluated as a function of T and ρ using the real-gas formulation of Reynolds.[9] The equation for Z can be derived from the sum of the partial pressures of CO_2 and N_2, $P = P_{CO_2} + P_{N_2}$,

$$P = Z_{CO_2} X_{CO_2} \rho \bar{R} T \big/ M_{CO_2} + Z_{N_2} X_{N_2} \rho \bar{R} T \big/ M_{N_2} \tag{2}$$

where $X_i \rho = \rho_i$, $M_{CO_2} = 44.01$ kJ/kg-K and $M_{N_2} = 28.013$ kJ/kg-K. Thus, the pressure becomes

$$P = \rho T \bar{R} \left(Z_{CO_2} X_{CO_2} \big/ M_{CO_2} + Z_{N_2} X_{N_2} \big/ M_{N_2} \right) \tag{3}$$

Using the relation between mole fraction and mass fraction ($Y_i = X_i M / M_i$), one obtains

$$P = (\rho \bar{R} T / M) \left(Y_{CO_2} Z_{CO_2} + Y_{N_2} Z_{N_2} \right) \tag{4}$$

so that

$$Z = Y_{CO_2} Z_{CO_2} + Y_{N_2} Z_{N_2} \tag{5}$$

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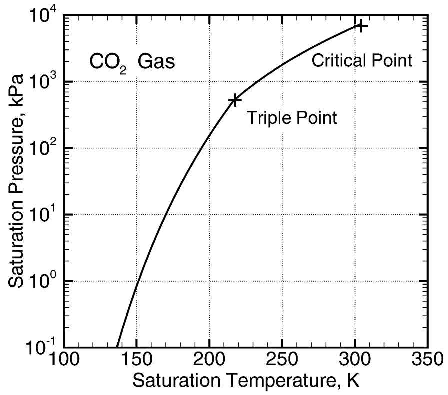

Fig. 1 Pressure-temperature diagram for CO$_2$, showing the saturation line.

B. Saturation Pressure

Reynolds[9] and Span and Wagner[10] present equations for the liquid-vapor saturation pressure of CO$_2$ for states between the triple point and the critical point. The equation for the saturated liquid-vapor line taken from Span and Wagner[10] is

$$\ln(P_s/P_c) = (T_c/T)\left(a_1 B + a_2 B^{1.5} + a_3 B^2 + a_4 B^4\right) \tag{6}$$

where $B = 1 - T/T_c$, $a_1 = -7.0602087$, $a_2 = 1.9391218$, $a_3 = -1.6463597$, and $a_4 = -3.2995634$. The values of P_c and T_c for CO$_2$ are 7377.3 kPa and 304.128 K, respectively.

For temperatures below the CO$_2$ triple point, the equation for the saturated solid-vapor (sublimation) line is given by Span and Wagner[10] as

$$\ln(P_s/P_{\text{tp}}) = (T_{\text{tp}}/T)\left(b_1 A + b_2 A^{1.9} + b_3 A^{2.9}\right) \tag{7}$$

where $A = 1 - T/T_{\text{tp}}$, $b_1 = -14.740846$, $b_2 = 2.4327015$, and $b_3 = -5.3061778$. The values of P_{tp} and T_{tp} for CO$_2$ are 517.95 kPa and 216.592 K, respectively. Equation (7) is accurate for $85\ \text{K} \le T \le T_{\text{tp}}$. Equations (6) and (7) give $P_s(T_s)$; if $T_s(P_s)$ is needed, the equations can be solved for T_s at a given value of P_s by iteration.

Figure 1 gives P_s as a function of T_s for CO$_2$ gas [data generated from Eqs. (6) and (7)]. Sublimation occurs at pressure-temperature states below the triple point, and vaporization occurs at pressure-temperature states between the triple point and the critical point.

The saturation states of N$_2$ are at such low temperatures and pressures ($T_{\text{tp}} = 63.15$ K and $P_{\text{tp}} = 12.53$ kPa) that they are not important in the present study. N$_2$ will be a gas for all of the pressures and temperatures of interest.

C. CO$_2$ and N$_2$ Properties

Thermodynamic properties for CO$_2$ and N$_2$ are developed using the formulation of Reynolds.[9] The pressure for each gas is written in the general form

$$P = \rho R T + \sum_{j=1}^{N} C_j(T) H_j(\rho) \tag{8}$$

where $C_j(T)$ is a polynomial in T, $H_j(\rho)$ is a polynomial in ρ, and N is the number of terms. Now if $C'_j = \mathrm{d}C_j/\mathrm{d}T$ and

$$I_j = \int_0^{\rho} \frac{1}{\rho^2} H_j(\rho)\,\mathrm{d}\rho$$

the equation for internal energy can be written as

$$u = \int_{T_{\text{tp}}}^{T} c_v^{\circ}(T)\,\mathrm{d}T + \sum_{j=1}^{N} [C_j - T C'_j] I_j + u_{\text{tp}} \tag{9}$$

where u_{tp} is the value of internal energy at T_{tp} ($u_{\text{tp}} = 321.7410$ kJ/kg for CO$_2$, $= 196.6228$ kJ/kg for N$_2$) and $c_v^{\circ}(T)$ is the thermally perfect, ideal-gas specific heat at constant volume (see Ref. 9 for the function). The summation term represents the deviation of u from its ideal-gas value. Enthalpy is defined as $h = u + P/\rho$.

The equation for entropy is

$$s = \int_{T_{\text{tp}}}^{T} \frac{c_v^{\circ}(T)}{T}\,\mathrm{d}T - R \ln \rho - \sum_{j=1}^{N} C'_j I_j + s_{\text{tp}} \tag{10}$$

where s_{tp} is the entropy at T_{tp} and $\rho \approx 0$ ($s_{\text{tp}} = 2.1396$ kJ/kg-K for CO$_2$, $= 3.2881$ kJ/kg-K for N$_2$). The second and third terms represent the effect of $\rho \neq \rho_{\circ}$ and the deviation from an ideal gas, respectively.[9]

Data are generated and presented in terms of W, where

$$W = \frac{m_{\text{N}_2}}{m_{\text{CO}_2}} = \frac{\rho_{\text{N}_2}}{\rho_{\text{CO}_2}} = \frac{P_{\text{N}_2} Z_{\text{CO}_2} M_{\text{N}_2}}{P_{\text{CO}_2} Z_{\text{N}_2} M_{\text{CO}_2}} \tag{11}$$

Replacing the partial pressures by mole fractions, one has

$$W = \frac{Y_{\text{N}_2} Z_{\text{CO}_2} M_{\text{N}_2}}{Y_{\text{CO}_2} Z_{\text{N}_2} M_{\text{CO}_2}} \tag{12}$$

Thus, using the relation $Y_{\text{CO}_2} + Y_{\text{N}_2} = 1$, one can write the mole fractions in terms of W as

$$Y_{\text{CO}_2} = F/(W + F), \qquad Y_{\text{N}_2} = W/(W + F) \tag{13}$$

where $F = Z_{\text{CO}_2} M_{\text{N}_2} / Z_{\text{N}_2} M_{\text{CO}_2}$.

The equations developed in this section were used to calculate the Mars atmospheric data for $0.1 \le P \le 1$ kPa and $150 \le T \le 300$ K, and the property data are presented in psychrometric chart form.

Table 1 Saturation thermodynamic data, *P* = 0.6266 kPa

T, K	W, kg$_{\text{N}_2}$/ kg$_{\text{CO}_2}$	Y_{CO_2}	v, m^3/ kg$_{\text{CO}_2}$	h, kJ/ kg$_{\text{CO}_2}$	s, kJ/ K-kg$_{\text{CO}_2}$	Z
147.94	0.0000	1.000	44.59	313.3	2.656	0.9997
147.80	0.0127	0.981	45.44	317.1	2.740	0.9997
147.60	0.0319	0.952	46.72	322.8	2.858	0.9997
147.40	0.0518	0.925	48.05	328.7	2.977	0.9997
147.20	0.0724	0.898	49.42	334.7	3.097	0.9997
147.00	0.0936	0.872	50.83	341.0	3.219	0.9997
146.80	0.1155	0.846	52.28	347.5	3.344	0.9998
146.60	0.1381	0.822	53.78	354.1	3.472	0.9998
146.40	0.1615	0.798	55.33	361.0	3.603	0.9998
146.20	0.1857	0.774	56.93	368.2	3.738	0.9998
146.00	0.2107	0.751	58.58	375.5	3.877	0.9998
145.80	0.2365	0.729	60.29	383.1	4.019	0.9998
145.60	0.2632	0.707	62.04	391.0	4.166	0.9998
145.40	0.2908	0.686	63.86	399.1	4.317	0.9998
145.20	0.3193	0.666	65.73	407.5	4.472	0.9998
145.00	0.3488	0.646	67.67	416.1	4.633	0.9998

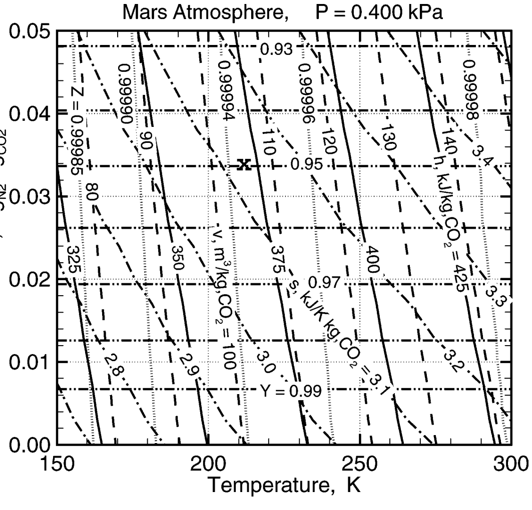

Fig. 2 Mars atmospheric thermodynamic properties at *P* = 0.40 kPa.

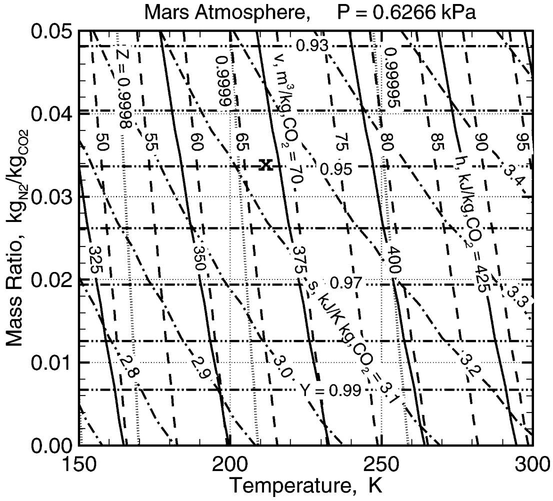

Fig. 3 Mars atmospheric thermodynamic properties at *P* = 0.6266 kPa.

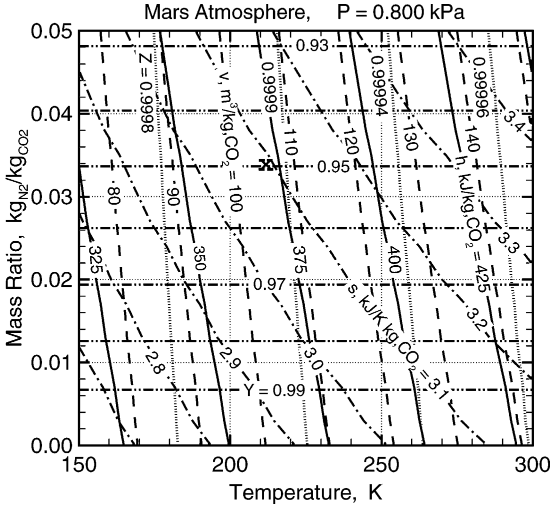

Fig. 4 Mars atmospheric thermodynamic properties at *P* = 0.80 kPa.

III. Results and Discussion

Thermodynamic properties of the Mars atmosphere have been calculated at several pressures. Table 1 gives data on the saturation line at the surface of Mars ($P = 0.6266$ kPa).

Contour plots for v, h, s, Y_{CO_2}, and Z were made in the W-T orthogonal coordinate system. Each property was plotted on a single frame, which was transparent, and the frames were stacked on top of each other to form the figure. Thus, each figure consists of five frames stacked on top of each other. The top four frames are transparent, so that the lines on all five frames can be seen.

The Mars surface temperature and pressure vary daily and seasonally. Figures 2–4 present a range of thermodynamic property data in psychrometric chart form for $P = 0.40$, 0.6266, and 0.80 kPa. The figures show enthalpy, specific volume, and entropy, in units of per kilogram of CO$_2$, Z, and Y_{CO_2} as a function of W and T for a specific value of P. Figure 3 shows the data at the Mars surface pressure of 0.6266 kPa. Figures 2 and 4 show data at pressures below and above the Mars surface pressure to cover the expected pressure variation.

The figures are complicated because of the number of properties. Constant h lines in units of kJ/kg$_{CO_2}$ are shown as solid lines. Constant v lines in units of m^3/kg$_{CO_2}$ are shown as dashed lines. Constant s lines in units of kJ/K-kg$_{CO_2}$ are shown as dot-dashed lines. Constant Z lines are shown as dotted lines. Constant Y_{CO_2} lines are shown as dot-dot-dashed lines. The constant h lines and constant v lines are almost vertical and almost parallel to each other. The constant s lines have about a −45-deg slope. The constant Z lines are approximately vertical, while the constant Y_{CO_2} lines are horizontal. One can convert the properties from per kg$_{CO_2}$ to per kg by multiplying by X_{CO_2}, where $X_{CO_2} = Y_{CO_2} M_{CO_2} / M$.

The generally accepted sea-level state for the Mars atmosphere is denoted by a bold X on the figures. The value of Y_{CO_2} in the Martian atmosphere is assumed to be 0.95, which corresponds to $W \approx 0.0336$ kg$_{N_2}$/kg$_{CO_2}$. The saturated solid-vapor state for the standard Mars atmosphere ($P = 0.6266$ kPa) occurs at $T \approx 145$ K, which is just below the left-hand side of Fig. 3.

Note that Z is essentially equal to one for the entire range of W and T. This implies that the ideal-gas approximation could be used to calculate the Mars atmospheric properties.

IV. Conclusions

The Mars atmospheric temperature and pressure values are much smaller than Earth values at the same altitude. The lower Mars atmosphere is essentially an ideal-gas mixture composed of 95% CO$_2$ and 5% N$_2$ by volume. Real-gas effects are shown to be negligible. The surface pressure and temperature are such that N$_2$ always remains in a gaseous state. The freezing and thawing of the CO$_2$ is a sublimation process, because of the low surface pressure on Mars. Data are developed and presented for the thermodynamic properties (enthalpy, specific volume, entropy, and compressibility) of the lower part of the Mars atmosphere as a function of temperature, mole fraction of CO$_2$, and mass ratio of N$_2$ to CO$_2$ for three representative Mars surface-pressure values.

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