

Carbon Dioxide Thermodynamic Properties Handbook

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Carbon Dioxide Thermodynamic Properties Handbook

**Covering Temperatures from -20° to 250°C
and Pressures up to 1000 bar**

Sara Anwar and John J. Carroll

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Calgary, Alberta, Canada



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Sara dedicates this book to her parents, Anwar Alam and Arjumand Bano.

In addition both authors would like to dedicate this book to their co-workers at Gas Liquids Engineering.

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Preface

Like water, carbon dioxide is one of the most studied substances in the annals of science. It has a readily accessible critical point (30.98°C and 73.77 bar), and it is relatively safe (compared with hydrocarbons and toxic chemicals such as hydrogen sulfide). The measurements have been critically reviewed and complex, highly accurate equations of state have been developed.

In the 21st century carbon dioxide has become an important social chemical. It has been implicated in global climate change, and governments are scrambling to deal with emissions of CO₂ to the environment, including taxing emitters. Carbon dioxide may one day rival other commodities.

This is the most comprehensive collection of data on the thermodynamic properties of carbon dioxide ever published, and much of this information is now no longer available in such a ready format anywhere else. The authors hope that this volume will become a standard reference work for engineers, chemists, and scientists everywhere, who are studying, working with, or hoping to combat carbon dioxide.

Introduction

Presented in this book are tabulated properties for pure carbon dioxide. The properties are based on the equation of state of Span and Wagner (1996). Although Span and Wagner (1996) also included tabular properties, the properties given here are at fine intervals of temperature and pressure and make rapid interpretation much easier.

The range of temperatures and pressure was selected as being appropriate for the application of carbon dioxide sequestration. However, the tabulated data are not limited to that application.

The first tables in this book are for the properties of saturated carbon dioxide. The pressures, therefore, that are given in these tables are the vapor pressure of pure CO₂ and they end at the critical point. One thing that looks unusual is that the heat capacity, C_p , is infinite at the critical point, but this is true by definition.

Derived Properties

From the tables provided in this book several other properties can be calculated directly. This section provides the formulae to perform these calculations.

Molar Volume

The molar volume, v , is basically the reciprocal of the density and can be calculated using the following definition:

$$v = \frac{M}{\rho} \quad (1)$$

where: v is the molar volume, m³/kmol
 M is the molar mass of carbon dioxide, 44.010 kg/kmol
 ρ is the density, kg/m³

Compressibility Factor

The compressibility factor, z , can be calculated from the values in the density tables using the following definition:

$$z = \frac{M P}{\rho R (t + 273.15)} \quad (2)$$

where: z is the compressibility factor, dimensionless
 M is the molar mass of carbon dioxide, 44.010 kg/kmol
 P is the total pressure, bar
 ρ is the density, kg/m³
 R is the universal gas constant, 0.083 145 bar•m³/kmol•K
 T is the temperature, °C

Specific Properties

The tabulated values for the enthalpy, entropy, and heat capacity are on a molar basis. In order to convert them to the specific property (per unit mass), divide by the molar mass of carbon dioxide (44.010 g/mol).

$$H = h/M$$

where: H is the specific enthalpy, kJ/kg
 h is the molar enthalpy, kJ/kmol (or J/mol)
 M is the molar mass of carbon dioxide, 44.010 kg/kmol

$$S = s/M$$

where: S is the specific entropy, kJ/kg•K
 s is the molar entropy, kJ/kmol•K (or J/mol•K)
 M is the molar mass of carbon dioxide, 44.010 kg/kmol

$$C_p = C_p/M$$

where: C_p is the specific heat capacity, kJ/kg•K
 C_p is the molar heat capacity, kJ/kmol•K (or J/mol•K)
 M is the molar mass of carbon dioxide, 44.010 kg/kmol

Internal Energy

The internal energy, U , in kJ/kg can be calculated the following definition:

$$U = H - \frac{100 P}{\rho} \quad (3)$$

where: U is the specific internal energy, kJ/kg
 H is the specific enthalpy, kJ/kg
 P is the pressure, bar
 ρ is the density, kg/m³

Alternatively, the molar internal energy, u , in J/mol can be calculated from:

$$u = h - \frac{1000 M P}{\rho} \quad (4)$$

where: u is the molar internal energy, J/mol
 M is the molar mass of carbon dioxide, 44.010 kg/kmol
 h is the molar enthalpy, J/mol

Linear Interpolation

The tables provided are at fine grids of temperature and pressure. However, for more accurate calculations the tables should be interpolated. The grid is sufficiently fine that linear interpolation is satisfactory.

$$y = \left(\frac{y_1 - y_2}{x_1 - x_2} \right) (x - x_1) + y_1 \quad (5)$$

One must be careful not to interpolate across the vapor pressure.

Example 1

What is the enthalpy of carbon dioxide at 50°C and 6.25 bar?

Answer: From Table 9 at 50°C:

$$P = 6 \text{ bar} \quad h = 734.0 \text{ J/mol (point 1)}$$

$$P = 7 \text{ bar} \quad h = 698.4 \text{ J/mol (point 2)}$$

Interpolating:

$$\begin{aligned} y &= \left(\frac{734.0 - 698.4}{6 - 7} \right) (6.25 - 6) + 734.0 \\ &= \underline{725.1 \text{ J/mol}} \end{aligned}$$

Example 2

What is the enthalpy of carbon dioxide at 71.3°C and 18 bar.

Answer: From Table 9:

	17.5 bar	20 bar
71°C	1209.5 J/mol	1127.4 J/mol
72°C	1252.2 J/mol	1170.8 J/mol

Interpolate with the pressure

$$\begin{aligned} y &= \left(\frac{1209.5 - 1127.4}{17.5 - 20} \right) (18 - 17.5) + 1209.5 \\ &= \underline{1193.1 \text{ J/mol}} \end{aligned}$$

and

$$\begin{aligned} y &= \left(\frac{1252.2 - 1170.8}{17.5 - 20} \right) (18 - 17.5) + 1252.2 \\ &= \underline{1235.9 \text{ J/mol}} \end{aligned}$$

These interpolations are summarized in the following table:

	17.5 bar	18 bar	20 bar
71°C	1209.5 J/mol	<i>1193.1 J/mol</i>	1127.4 J/mol
72°C	1252.2 J/mol	<i>1235.9 J/mol</i>	1170.8 J/mol

Interpolate with the temperature (the italicized values in the above table).

$$\begin{aligned} y &= \left(\frac{1193.1 - 1235.9}{71 - 72} \right) (71.3 - 71) + 1193.1 \\ &= \underline{1205.9 \text{ J/mol}} \end{aligned}$$

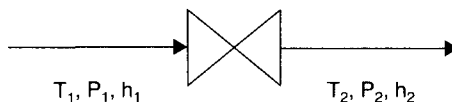


Fig. 1 Schematic of the Joule-Thomson Expansion

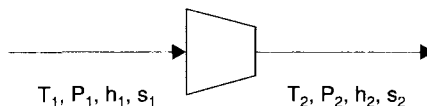


Fig. 2 Schematic of the Compression of a Gas Stream

Sample Calculations

Presented in this section are some sample calculations based on classical thermodynamics, which demonstrate some applications for the tables.

Joule-Thomson Expansion

One of the classic examples in thermodynamics is the expansion of a fluid across a valve (or a porous plug), which is a constant enthalpy process. The process is shown in Fig. 1. The specification of this process is given the temperature and the pressure of the inlet (state 1) and the pressure at the outlet (state 2), calculate the temperature of the outlet stream. Since this is an isenthalpic process, we also know that:

$$h_1 = h_2$$

Isentropic Compression

An ideal compressor is an isentropic process (i.e. the change in entropy of the stream is zero). A simple schematic of a compression process is shown in Fig. 2. The specification for a compressor is the inlet temperature and pressure and the outlet pressure (or equivalently the compression ratio). For the ideal case:

$$s_1 = s_2$$

Thus the outlet of the compressor is specified by P_2 and s_2 from which the other properties can be calculated.

The ideal, adiabatic work compression can then be calculated from the difference in the enthalpies:

$$w^* = h_2 - h_1$$

where w^* is the ideal, adiabatic work of compression, J/mol

Example 3

Calculate the temperature drop when a carbon dioxide stream is throttled from 7 bar and 50°C to 1 bar.

Answer: At 7 bar and 50°C the enthalpy is 698.4 J/mol (from Table 6). At 1 bar, from Table 6 we have the following:

Temperature	Enthalpy
44°C	678.2 J/mol•K
45°C	716.5 J/mol•K

By linear interpolation:

$$y = \left(\frac{44 - 45}{678.2 - 716.5} \right) (698.4 - 678.2) + 44$$

$$= \underline{44.5^\circ\text{C}}$$

So the exit temperature is 44.5°C, a cooling of about 5.5 Celsius degrees.

Example 4

The suction pressure is 3.5 bar and the temperature is 50°C. For a discharge pressure is 10 bar calculate the discharge temperature and the work of compression.

Answer: The flowing properties for carbon dioxide at 50°C at 3 and 4 bar are from Tables x and y and the value at 3.5 bar is interpolated from these values.

	3 bar	3.5 bar	4 bar
entropy	-6.214 J/mol•K	-7.448 J/mol•K	-8.682 J/mol•K
enthalpy	839.3 J/mol	821.9 J/mol	804.4 J/mol

From Table 11 at 10 bar, it can be seen that the discharge temperature is between 130° and 131°C, because the entries in the table span the entropy value at 50°C and 3.5 bar (-7.448 J/mol K). In fact, from these values it can be seen that the discharge temperature is almost exactly 131°C. For many cases this may be sufficiently accurate.

However the values for the entropy can be used to interpolate the temperature more accurately as shown below:

	130°C	130.99°C	131°C
entropy	-7.583 J/mol•K	-7.448 J/mol•K	-7.447 J/mol•K
enthalpy	3916.2 J/mol	3958.4 J/mol	3958.8 J/mol

$$y = \left(\frac{130 - 131}{-7.583 - -7.447} \right) (-7.583 - -7.448) + 130$$

$$= \underline{130.99^\circ\text{C}}$$

Finally the ideal, adiabatic work of compression is the change in enthalpy:

$$w^* = 3958.4 - 821.9 = \underline{3136.5 \text{ J/mol}}$$

Conversion factors

From	To	Multiply by
kg	lb	2.20462
m ³	ft ³	35.3147
kg/m ³	lb/ft ³	0.062428
J/mol	Btu/lb-mol	0.429923
kJ/kg	Btu/lb	0.429923
J/mol•K	Btu/lb-mol•R	0.238846
kJ/kg•K	Btu/lb•R	0.238846
bar	kPa	100
bar	MPa	0.1
bar	psia	14.5038

Temperature: $t/^{\circ}\text{F} = (t/^{\circ}\text{C}) \times 9/5 + 32$

$$-20^{\circ}\text{C} = -4^{\circ}\text{F}$$

$$-10^{\circ}\text{C} = 14^{\circ}\text{F}$$

$$0^{\circ}\text{C} = 32^{\circ}\text{F}$$

$$10^{\circ}\text{C} = 50^{\circ}\text{F}$$

$$20^{\circ}\text{C} = 68^{\circ}\text{F}$$

$$30^{\circ}\text{C} = 86^{\circ}\text{F}$$

$$50^{\circ}\text{C} = 122^{\circ}\text{F}$$

$$100^{\circ}\text{C} = 212^{\circ}\text{F}$$

$$150^{\circ}\text{C} = 302^{\circ}\text{F}$$

$$200^{\circ}\text{C} = 392^{\circ}\text{F}$$

$$250^{\circ}\text{C} = 482^{\circ}\text{F}$$

Reference

Span, R. and W. Wagner, "A New Equation of State for Carbon Dioxide Covering the Fluid Region from the Triple-Point Temperature to 1100 K at Pressures up to 800 MPa", *J. Phys. Chem. Ref. Data*, **25**, 1509–1596, (1996).