STANFORD
AERONAUTICS &
ASTRONAUTICS

AA210A

Fundamentals of Compressible Flow

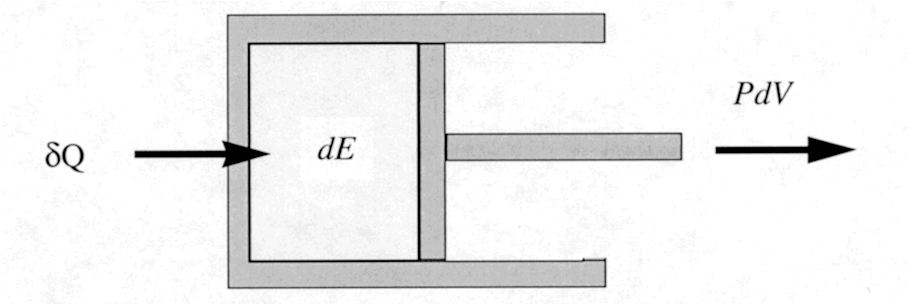
Chapter 2 -Thermodynamics of dilute gases

2.1 Introduction

The power of thermodynamics comes from the fact that the change in the state of a fluid is independent of the actual physical process by which the change is achieved; thermodynamic theory is expressed in terms of perfect differentials.

2.2 Thermodynamics

Piston-cylinder combination.



First law of thermodynamics.

$$\delta Q = dE + \delta W .$$

$$\delta Q = dE + PdV$$

The work done by the system is the mechanical work by a force acting over a distance.

$$PdV = (F/A)d(Ax) = Fdx$$

When dealing with fluid flows it is convenient to work in terms of intensive (per unit mass) variables.

$$\delta q = de + Pdv$$

If there is an equation of state for the substance inside the cylinder the first law is

$$\delta q = de + P(e, v)dv$$

According to Pfaff's theorem there must exist an integrating factor such that the first law becomes a perfect differential.

$$\frac{\delta q}{T(e,v)} = \frac{de}{T(e,v)} + \frac{P(e,v)}{T(e,v)}dv = ds(e,v)$$

Once one accepts the first law and the existence of an equation of state then two new variables of state are implied; an integrating factor, the temperature, and an associated integral called entropy. The final result is the famous Gibbs equation which is the starting point for the field of thermodynamics

$$\boxed{Tds = de + Pdv}$$

The partial derivatives of the entropy are

$$\left.\frac{\partial s}{\partial e}\right|_{v\ =\ constant} = \frac{1}{T(e,v)} \qquad \left.\frac{\partial s}{\partial v}\right|_{e\ =\ constant} = \frac{P(e,v)}{T(e,v)}.$$

2.3 The Carnot Cycle

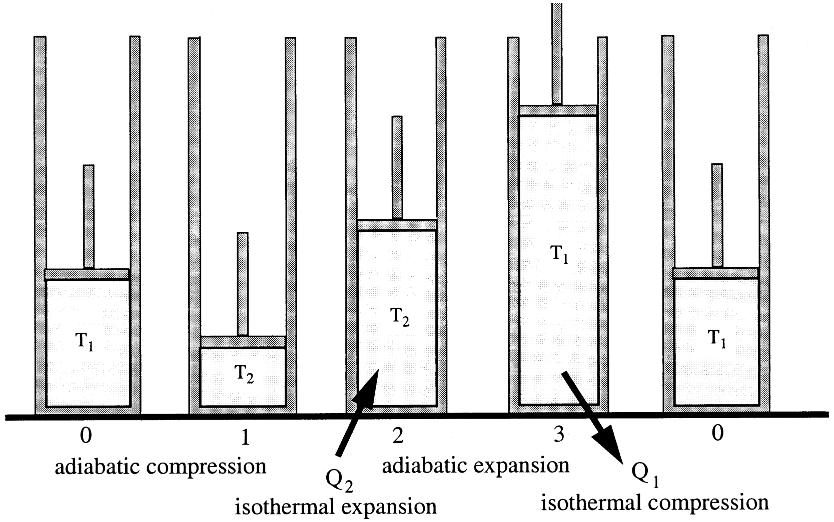


Figure 2.2 The Carnot Cycle heat engine

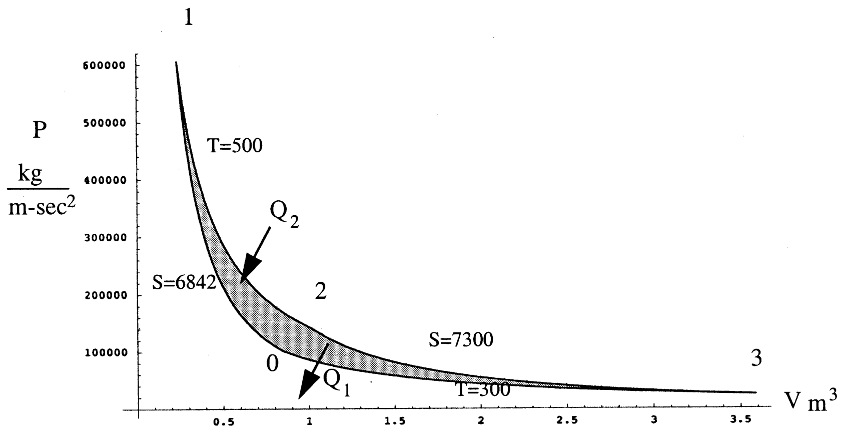


Figure 2.3 P-V diagram of the Carnot Cycle

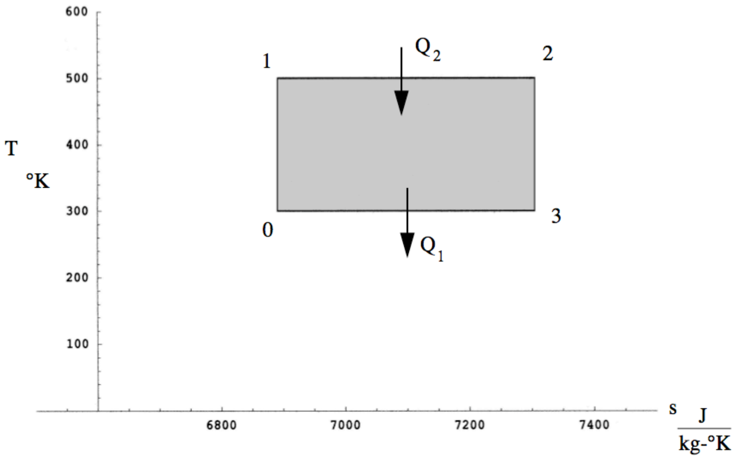


Figure 2.4 T-S diagram of the Carnot cycle

Thermodynamic efficiency of the cycle

$$\eta = \frac{\textit{work output by the system during the cycle}}{\textit{heat added to the system during the cycle}} = \frac{W}{Q_2}$$

First Law $$\delta Q = dE + \delta W .$$

Over the cycle the change in internal energy is zero and the work done is

$$W = Q_2 + Q_1$$

So the efficiency is

$$\eta = 1 + \frac{Q_1}{Q_2} .$$

Since the temperature is constant during the heat interaction

$$\frac{Q_1}{T_1} = -\frac{Q_2}{T_2}$$

$$\oint ds = \oint \frac{\delta q}{T} = \frac{Q_1}{T_1} + \frac{Q_2}{T_2} = 0$$

Finally

$$\eta_C = 1 - \frac{T_1}{T_2} < 1$$

2.3.1 The absolute scale of temperature

For any Carnot cycle regardless of the working fluid

$$\frac{Q_1}{Q_2} = -\frac{T_1}{T_2}.$$

This relation enables an absolute scale of temperature to be defined that is independent of the properties of any particular substance.

There is an arbitrary scale factor in the definition of the temperature. The convention is to put the freezing point of water exactly at 273.15 Kelvin. Two scales are widely used and they are related by

$$T_{Rankine} = \left(\frac{9}{5}\right) T_{Kelvin}.$$

$$T_{Rankine} = T_{Farenheit} + 459.67$$

$$T_{Kelvin} = T_{Centigrade} + 273.15.$$

2.4 Enthalpy

It is often useful to exchange dependent and independent variables. Define the enthalpy.

$$h = e + Pv$$

In terms of the enthalpy, the Gibbs equation becomes

$$ds = \frac{dh}{T} - \frac{v}{T}dP$$

In this way the pressure has been converted to an independent variable.

$$ds(h, P) = \frac{dh}{T(h, P)} - \frac{v(h, P)}{T(h, P)}dP$$

The partial derivatives of the entropy are

$$\left.\frac{\partial s}{\partial h}\right|_{P = constant} = \frac{1}{T(h, P)} \qquad \left.\frac{\partial s}{\partial P}\right|_{h = constant} = -\frac{v(h, P)}{T(h, P)}$$

By defining additional variables of state and rearranging the Gibbs equation suitably, any variable of state can be expressed in terms of any two others.

$$
\begin{aligned}
e &= \phi(T, P) \;; & s &= \zeta(T, v) \\
g &= \xi(e, P) \;; & h &= \varphi(T, P) \\
s &= \theta(h, P) \;; & s &= \beta(e, v)
\end{aligned}
$$

2.4.1 Gibbs equation on a fluid element

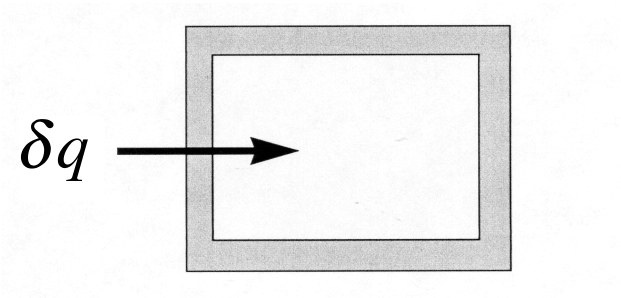
We will often use the Gibbs equation to describe the thermodynamic state of a fluid element moving in a flow.

$$\frac{Ds}{Dt} = \frac{1}{T}\frac{Dh}{Dt} - \frac{1}{\rho T}\frac{DP}{Dt}$$

or

$$\frac{Ds}{Dt} = \frac{1}{T}\frac{De}{Dt} - \frac{1}{\rho^2 T}\frac{D\rho}{Dt}$$

2.5 Heat capacities

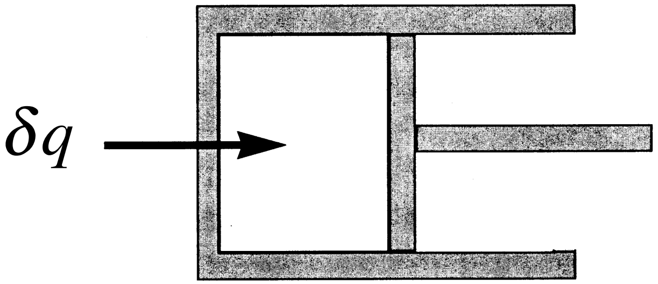


Heat capacity at constant volume.

$$\delta q = de(T,v) + P(T,v)dv = \left(\left. \frac{\partial e}{\partial T} \right|_{v=const} \right) dT + \left(\left. \frac{\partial e}{\partial v} \right|_{T=const} \right) dv + P(T,v)dv$$

$$dv = 0$$

$$C_v = \left. \frac{\delta q}{dT} \right|_{v=const} = \left(\left. \frac{\partial e}{\partial T} \right|_{v=const} \right)$$



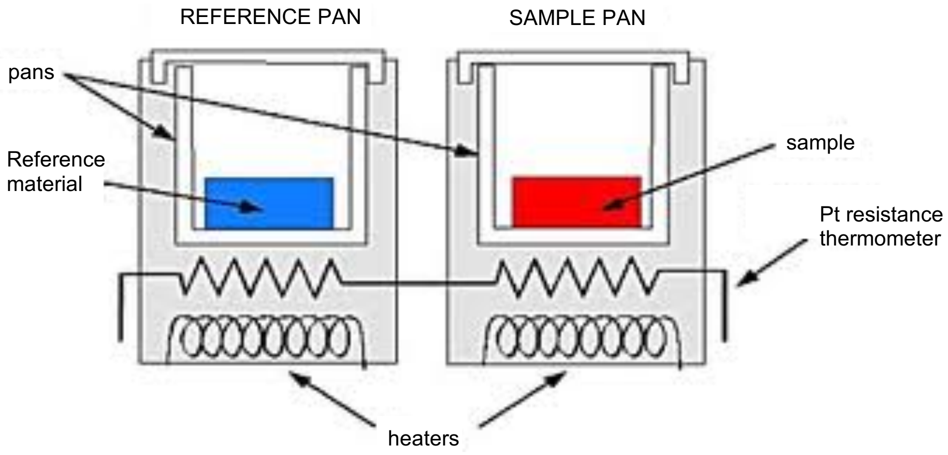
Heat capacity at constant pressure.

$$\delta q = dh(T,P) - v(T,P)\,dP = \left(\left.\frac{\partial h}{\partial T}\right|_{P=const}\right)dT + \left(\left.\frac{\partial h}{\partial P}\right|_{T=const}\right)dP - v(T,P)\,dP$$

$$dP = 0$$

$$C_p = \left.\frac{\delta q}{dT}\right|_{P=const} = \left(\left.\frac{\partial h}{\partial T}\right|_{P=const}\right)$$

One way to measure heat capacity is to use a Differential Scanning Calorimeter



The energy needed to maintain the reference and test sample at the same temperature is measured enabling the heat capacity of the test sample to be determined.

Enthalpy of a general substance.

$$h(T,P)=\int^{T} C_p(T,P)\,dT+f(P)$$

Typically the heat capacity and enthalpy are tabulated as functions of temperature at a standard pressure of $10^5\,N/m^2$.

The standard enthalpy of a substance at temperature T is.

$$h^{\circ}(T)=\int_{0}^{T_{fusion}} C^{\circ}_p(T)\,dT+\Delta H^{\circ}_{fusion}+\int_{T_{fusion}}^{T_{vaporization}} C^{\circ}_p(T)\,dT+\Delta H^{\circ}_{vaporization}+\int_{T_{vaporization}}^{T} C^{\circ}_p(T)\,dT$$

2.6 Ideal gases (also called perfect gases)

Ideal (perfect) gas equation of state

$$P = \frac{nR_uT}{V}$$

Universal gas constant

$$R_u = 8314.472\ Joules/(kgmole - K)$$

The ideal (perfect) gas law in terms of the density

$$\boxed{P = \rho RT}$$

where

$$R = R_u / M_w$$

For Air the gas constant is

$$\left.\begin{aligned} M_w\big|_{air} &= 28.9644 \ \ kilograms/kmole \\ R &= 287.06 \ \ m^2/sec^2 - K \end{aligned}\right\}$$

The perfect gas equation of state implies that the heat capacity, internal energy and enthalpy depend only on temperature.

$$h(T) = e + P/\rho = e(T) + RT$$

For ideal gases we can determine the internal energy and enthalpy using

$$de = C_v(T)dT \quad ; \qquad dh = C_p(T)dT$$

The gas constant can be expressed in terms of the heat capacities.

$$RdT = dh - de = (C_p - C_v)dT$$

$$R = C_p - C_v$$

The ratio of specific heats is a key parameter characterizing a gas.

$$\gamma = \frac{C_p}{C_v}$$

The ideal gas model has two basic assumptions:

1) The gas is composed of colliding molecules with negligible volume.
2) The force between particles is negligible.

In real gases the volume of the molecules becomes important at high densities and there are van der Waals forces between molecules that act at short distances.

These effects are accounted for in the van der Waals equation of state.

$$P = \rho RT\left(\frac{1}{1-b\rho} - \frac{a\rho}{RT}\right)$$

$$\frac{a}{b} = \frac{27}{8}RT_c \quad , \qquad \frac{a}{b^2} = 27P_c$$

2.7 Constant specific heat

For monatomic gases such as helium the heat capacity is constant over a very wide range of temperatures from very low temperatures close to vaporization up to ionization temperatures.

The heat capacity of diatomic gases such as nitrogen is nearly constant within a certain range of temperatures well above the vaporization temperature and well below combustion temperatures.

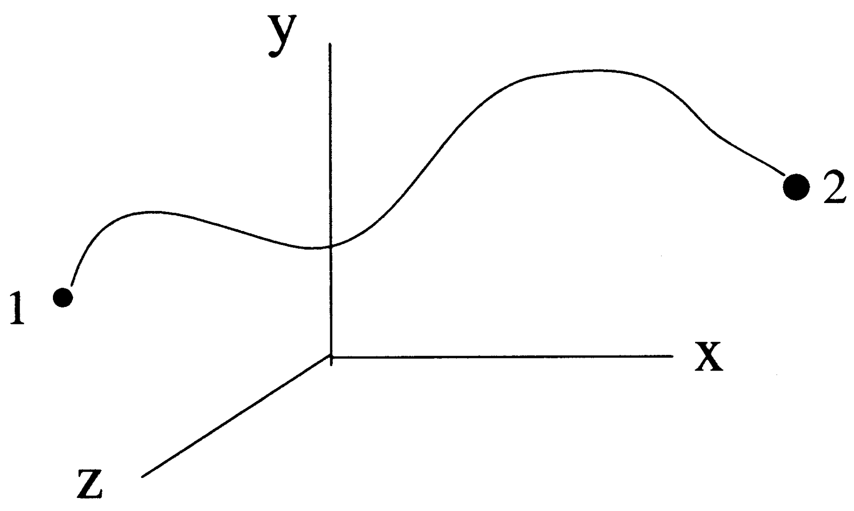
It is often convenient to assume that the heat capacity is constant over the temperature range of interest. Under this assumption the gas is said to be *calorically perfect*.

For constant heat capacity the Gibbs equation

$$\frac{ds}{C_v} = \left(\frac{dT}{T}\right) - (\gamma - 1)\left(\frac{d\rho}{\rho}\right)$$

can be easily integrated.

Consider a parcel of gas that moves between two points in a flow.



The integrated Gibbs equation in terms of temperature and density

$$exp\left(\frac{s_2 - s_1}{C_v}\right) = \left(\frac{T_2}{T_1}\right)\left(\frac{\rho_2}{\rho_1}\right)^{-(\gamma - 1)}.$$

or equivalently

$$ds = \frac{dh}{T} - \left(\frac{1}{\rho T}\right)dp = C_p\frac{dT}{T} - R\frac{dp}{p}.$$

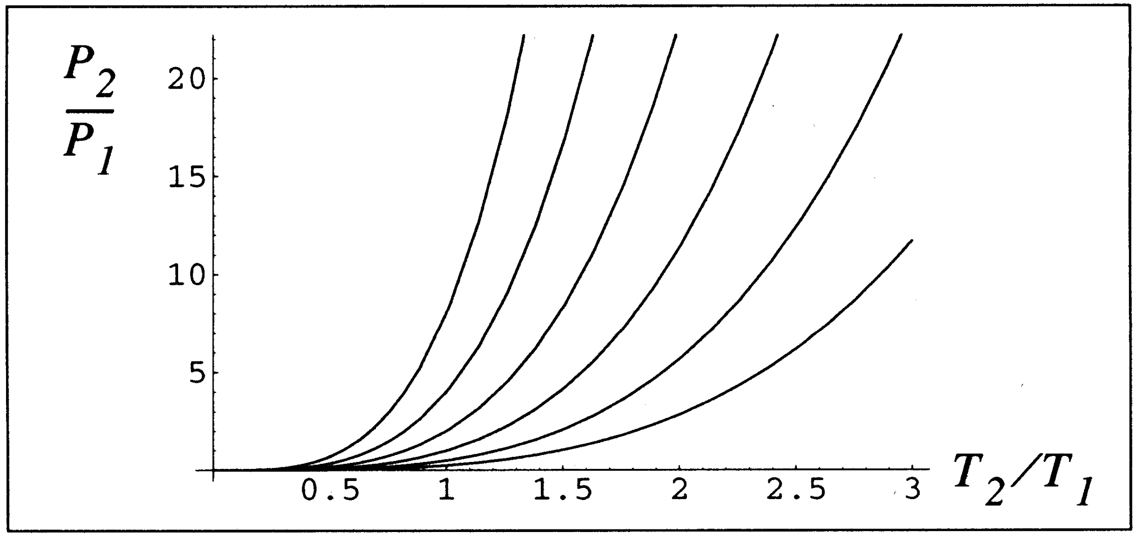
The integrated Gibbs equation in terms of temperature and pressure

$$\exp\left(\frac{s_2 - s_1}{C_p}\right) = \left(\frac{T_2}{T_1}\right)\left(\frac{P_2}{P_1}\right)^{-\left(\frac{\gamma - 1}{\gamma}\right)}.$$

The integrated Gibbs equation in terms of pressure and density

$$\exp\left(\frac{s_2 - s_1}{C_v}\right) = \left(\frac{P_2}{P_1}\right)\left(\frac{\rho_2}{\rho_1}\right)^{-\gamma}.$$

Lines of constant entropy change



In an isentropic process

$$\frac{P_2}{P_1} = \left(\frac{T_2}{T_1}\right)^{\frac{\gamma}{\gamma-1}} ; \quad \frac{P_2}{P_1} = \left(\frac{\rho_2}{\rho_1}\right)^{\gamma} ; \quad \frac{\rho_2}{\rho_1} = \left(\frac{T_2}{T_1}\right)^{\frac{1}{\gamma-1}} .$$

These relations are sometimes called the *isentropic chain*

2.8 The entropy of mixing

2.8.1 Sample problem - thermal mixing – constant pressure

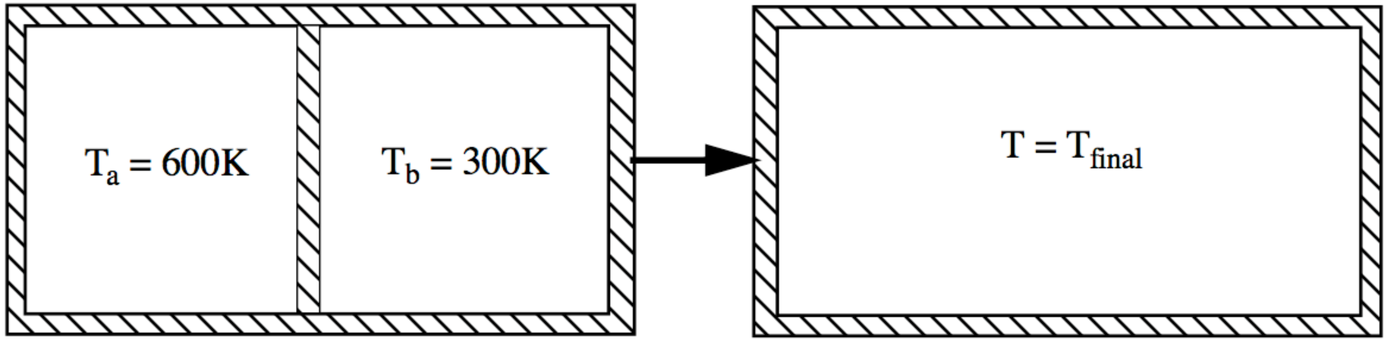


Figure 2.9 Thermal mixing of an ideal gas at two temperatures

Thermal energy

$$E - E_{ref} = m_a C_v (T_a - T_{ref}) + m_b C_v (T_b - T_{ref}) = (m_a + m_b) C_v (T_{final} - T_{ref})$$

$$m_a C_v T_a + m_b C_v T_b = (m_a + m_b) C_v T_{final}$$

From the ideal gas law

$$PV = m_a R T_a = m_b R T_b \qquad \frac{m_b}{m_a} = \frac{T_a}{T_b}$$

$$T_{final} = \frac{m_a T_a + m_b T_b}{(m_a + m_b)} = \frac{T_a + \left(\frac{m_b}{m_a}\right) T_b}{\left(1 + \frac{m_b}{m_a}\right)} = \frac{2 T_a T_b}{T_a + T_b} = 400K$$

For a constant pressure process

$$\frac{s_{final} - s_a}{C_p} = \ln\frac{T_{final}}{T_a}$$

$$\frac{s_{final} - s_b}{C_p} = \ln\frac{T_{final}}{T_b}$$

Entropy change of the system

$$\frac{s_{final} - s_{initial}}{C_p} = \frac{m_a\left(\frac{s_{final} - s_a}{C_p}\right) + m_b\left(\frac{s_{final} - s_b}{C_p}\right)}{m_a + m_b}$$

$$\frac{s_{final} - s_{initial}}{C_p} = \frac{ln\frac{T_f}{T_a} + \left(\frac{T_a}{T_b}\right) ln\frac{T_f}{T_b}}{1 + \left(\frac{T_a}{T_b}\right)} = \frac{ln\frac{400}{600} + (2)\, ln\frac{400}{300}}{1 + (2)}$$

$$\frac{s_{final} - s_{initial}}{C_p} = \frac{-0.405465 + 2(0.28768)}{3} = 0.0566$$

2.8.2 Entropy change due to mixing of distinct gases

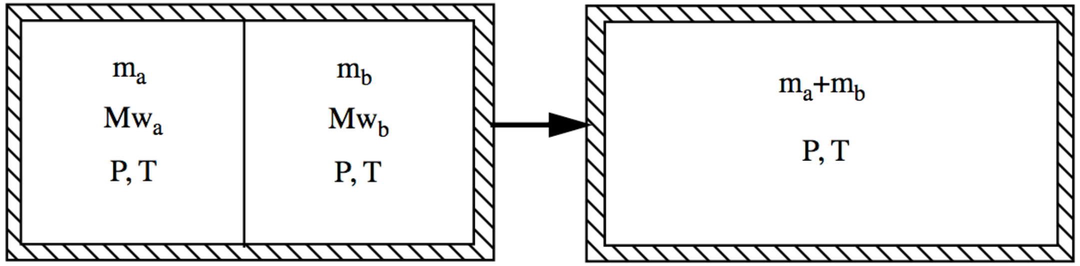


Figure 2.10 Mixing of two ideal gases at constant pressure and temperature

$$ds = C_p\frac{dT}{T} - R\frac{dP}{P}$$

Intensive entropy of each gas

$$s_a = \int C_{p_a}\frac{dT}{T} - \frac{R_u}{Mw_a}\ln P + \alpha_a$$

$$s_b = \int C_{p_b}\frac{dT}{T} - \frac{R_u}{Mw_b}\ln P + \alpha_b$$

Extensive entropy of the system

$$S = m_a s_a + m_b s_b$$

Define mass fractions

$$\chi_a = \frac{m_a}{m_a + m_b} \qquad \chi_b = \frac{m_b}{m_a + m_b}$$

Intensive entropy of the system before mixing

$$s_{before} = \frac{S_{before}}{m_a + m_b} = \chi_a s_a + \chi_b s_b$$

$$s_{before} = \chi_a\left(\int C_{p_a}\frac{dT}{T} - \frac{R_u}{Mw_a} \ln P + \alpha_a\right) + \chi_b\left(\int C_{p_b}\frac{dT}{T} - \frac{R_u}{Mw_b} \ln P + \alpha_b\right)$$

After mixing each gas fills the volume. Partial pressures after mixing are

$$P_a = \frac{m_a}{V}\frac{R_u}{Mw_a}T \qquad P_b = \frac{m_b}{V}\frac{R_u}{Mw_b}T$$

$$P = P_a + P_b$$

$$s_{after} = \chi_a\left(\int C_{p_a}\frac{dT}{T} - \frac{R_u}{Mw_a}\ln P_a + \alpha_a\right) + \chi_b\left(\int C_{p_b}\frac{dT}{T} - \frac{R_u}{Mw_b}\ln P_b + \alpha_b\right)$$

$$s_{after} - s_{before} = \chi_a\frac{R_u}{Mw_a}\ln\left(\frac{P}{P_a}\right) + \chi_b\frac{R_u}{Mw_b}\ln\left(\frac{P}{P_b}\right) > 0$$

2.9 Isentropic Expansion

2.9.1 Blowdown of a pressure vessel

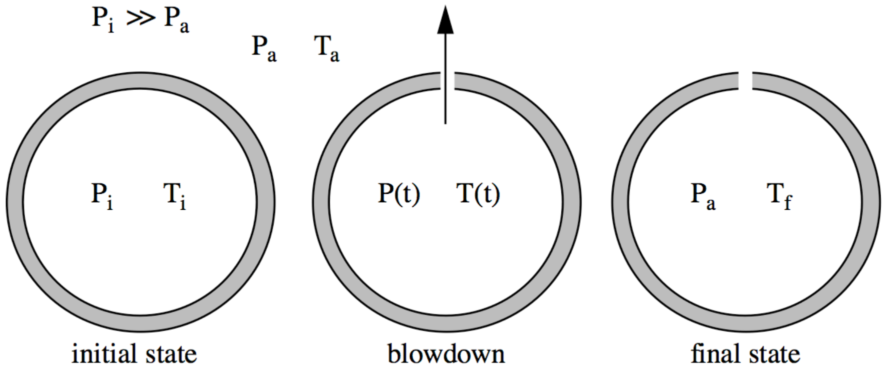
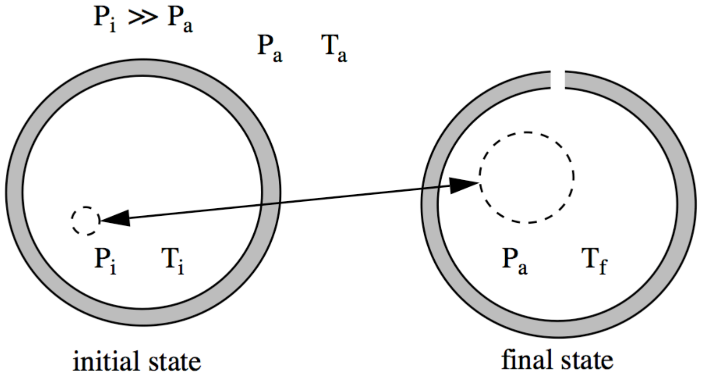


Figure 2.11 A spherical, thermally insulated pressure vessel exhausts to the surroundings through a small hole.



Final gas temperature inside the sphere

$$\frac{T_f}{T_i} = \left(\frac{P_a}{P_i}\right)^{\frac{\gamma - 1}{\gamma}} \tag{2.82}$$

Entropy change for the ejected gas

$$\frac{s_f - s_i}{C_p} = Log\left(\frac{T_a}{T_i}\right) - \left(\frac{\gamma - 1}{\gamma}\right) Log\left(\frac{P_a}{P_i}\right) \tag{2.83}$$

2.9.2 Work done by an expanding gas

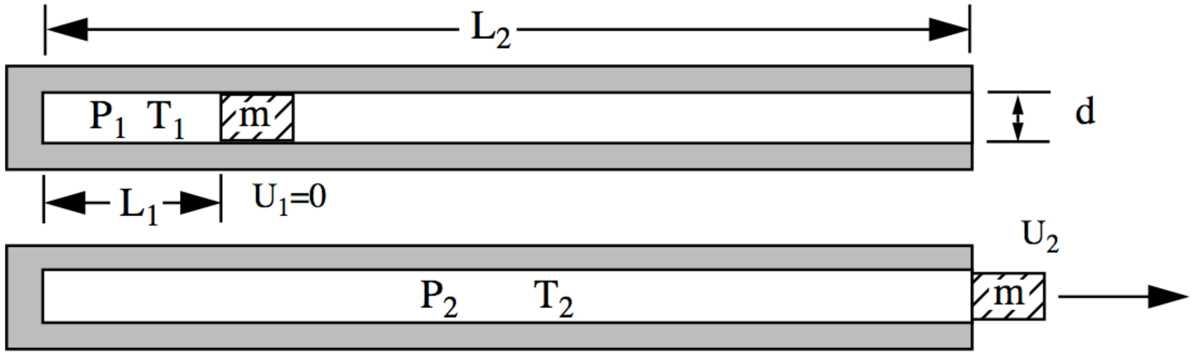


Figure 2.12 Projectile energized by an expanding gas

$$W = \int_{L_1}^{L_2} P dV = \frac{1}{2} m U_2^2 \tag{2.84}$$

$$\frac{P}{P_1} = \left(\frac{\rho}{\rho_1}\right)^{\gamma} = \left(\frac{\dfrac{4m_{gas}}{\pi d^2 L}}{\dfrac{4m_{gas}}{\pi d^2 L_1}}\right)^{\gamma} = \left(\frac{L_1}{L}\right)^{\gamma} \tag{2.85}$$

$$\frac{1}{2}mU_2^2 = \left(\frac{\pi d^2}{4}\right)\int_{L_1}^{L_2} P_1\left(\frac{L_1}{L}\right)^{\gamma} dL\,. \tag{2.86}$$

$$\frac{1}{2}mU_2^2 = \left(\frac{\pi d^2}{4}\right)\frac{P_1 L_1^{\gamma}}{1-\gamma}\left(L_2^{1-\gamma} - L_1^{1-\gamma}\right) \tag{2.87}$$

$$\frac{1}{2}mU_2^2 = \left(\frac{\pi d^2 L_1}{4}\right)\frac{P_1}{\gamma-1}\left(1 - \left(\frac{L_1}{L_2}\right)^{\gamma-1}\right) \tag{2.88}$$

$$V_1 = \frac{\pi d^2 L_1}{4}\,. \tag{2.89}$$

$$\frac{1}{2}mU_2^2 = \frac{P_1 V_1}{\gamma-1}\left(1 - \left(\frac{L_1}{L_2}\right)^{\gamma-1}\right) \tag{2.90}$$

$$\boxed{\frac{1}{2}mU_2^2 = m_{gas}C_v T_1\left(1 - \left(\frac{L_1}{L_2}\right)^{\gamma-1}\right)} \tag{2.91}$$

2.9.3 Example - Helium gas gun

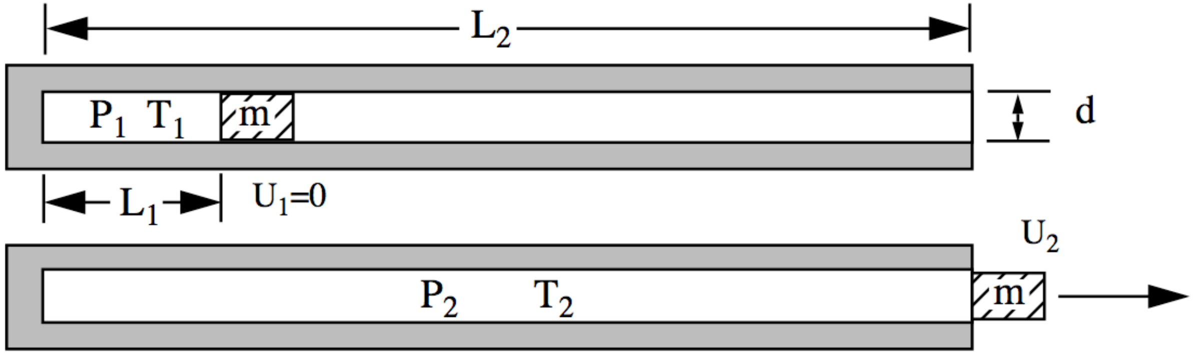


Figure 2.12 Projectile energized by an expanding gas

$P_1 = 4 \times 10^8 N/M^2$ $T_1 = 2000° K$ $L_2 = 2\ M$

$d = 0.04\ M$ $m = 0.1 kg$ $M_w = 4.0026$

$$P_1 V_1 = m_{gas}\left(\frac{R_u}{M_w}\right) T_1 . \tag{2.92}$$

$$m_{gas} = \frac{P_1 V_1}{T_1}\left(\frac{M_w}{R_u}\right) = \frac{4 \times 10^8}{2000}\left(\frac{\pi(0.04)^2(0.1)}{4}\right)\left(\frac{4.0026}{8314.472}\right) = 0.01208\ Kg \tag{2.93}$$

$$C_v = (3/2)R$$

$$U_2 = \left[2\left(\frac{0.01208}{0.1}\right)\left(\frac{3}{2}\right)\left(\frac{8314.472}{4.0026}\right)(2000)\left(1-\left(\frac{0.1}{2}\right)^{\frac{2}{3}}\right)\right]^{\frac{1}{2}} = 1140.7\ M/Sec\,. \qquad (2.94)$$

$$a_1 = \sqrt{\gamma R T_1} = 2631\ M/Sec\,. \qquad (2.95)$$

$$T_2 = T_1\left(\frac{L_1}{L_2}\right)^{\gamma-1} = 2000\left(\frac{0.1}{2}\right)^{2/3} = 271\ K\,. \qquad (2.96)$$

$$a_2 = \sqrt{\gamma R T_2} = 968\ M / \mathrm{Sec} \qquad (2.97)$$

2.10 Some results from statistical mechanics

Heat capacities of monatomic and diatomic gases are predicted very accurately using the theory of statistical mechanics which treats the gas as a very large ensemble of colliding particles.

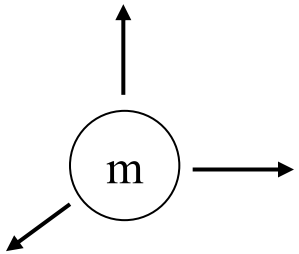
$$C_p = \frac{\beta + 2}{2}R \; ; \qquad C_v = \frac{\beta}{2}R \; ; \qquad \gamma = \frac{\beta + 2}{\beta}$$

Where beta is the number of degrees of freedom of the appropriate molecular model.

According to the Law of Equipartition each degree of freedom contains 1/2 kT of the energy of the molecule where k is Boltzmann's constant.

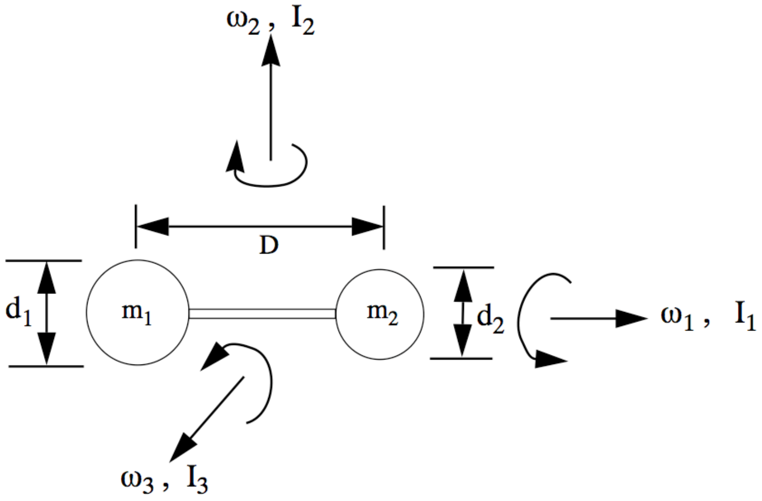
$$k = 1.38 \times 10^{-23}\, Joules/K$$

Molecular model of a gas



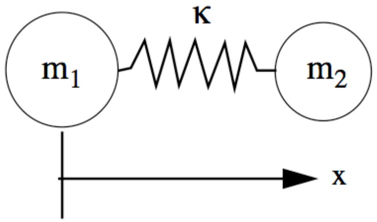
monatomic gas

$$E = \frac{1}{2}mu^2 + \frac{1}{2}mv^2 + \frac{1}{2}mw^2$$



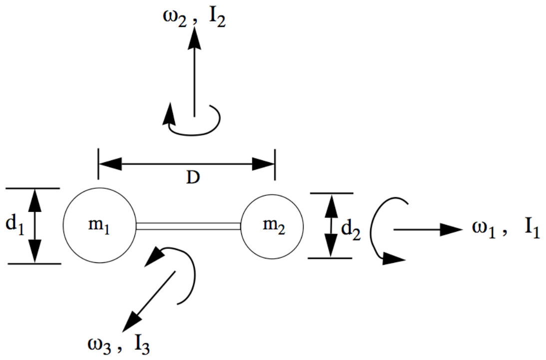
diatomic gas

$$E_{solid\ dumbell} = \cancel{\frac{1}{2}I_1\omega_1^2} + \frac{1}{2}I_2\omega_2^2 + \frac{1}{2}I_3\omega_3^2$$



$$E_{spring\text{-}mass} = \frac{1}{2}m_r\dot{x}^2 + \frac{1}{2}\kappa x^2$$

diatomic gas



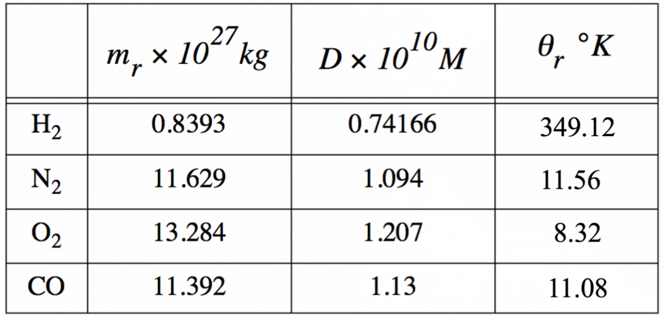
$$E_{solid\ dumbell} = \frac{1}{2}I_1\omega_1^2 + \frac{1}{2}I_2\omega_2^2 + \frac{1}{2}I_3\omega_3^2$$

$$h = 6.626 \times 10^{-34}\ J\text{-}sec$$

$$E_{2,\,3\,diatomic\ molecule} = \left(\frac{h}{2\pi}\right)^2 \frac{K(K+1)}{2I_{2,\,3}} = \left(\frac{h}{2\pi}\right)^2 \frac{K(K+1)}{2(m_r D^2)} \qquad K = 0,1,2,3\ldots$$

$$\frac{1}{2}k\theta_r \approx E_{2,\,3\,diatomic\ molecule}$$

$$\theta_r = \left(\frac{h}{2\pi}\right)^2 \frac{2}{k\,(m_r D^2)}$$



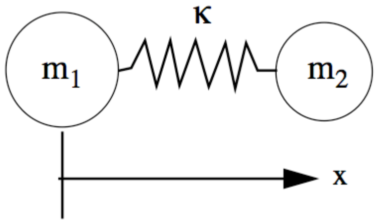
	$m_r \times 10^{27}\,kg$	$D \times 10^{10}\,M$	θ_r °K
H_2	0.8393	0.74166	349.12
N_2	11.629	1.094	11.56
O_2	13.284	1.207	8.32
CO	11.392	1.13	11.08

Figure A.12: *Rotational constants for several diatomic gases.*

$$E_{1\,diatomic\ molecule} = \left(\frac{h}{2\pi}\right)^2 \frac{K(K+1)}{2I_1}$$

$$\theta_{r1} = \left(\frac{h}{2\pi}\right)^2 \frac{2}{kI_1}$$

$$\theta_{r1\ electron\ cloud\ hollow\ sphere} \approx 3670\,\theta_r$$



$$E_{spring\text{-}mass} = \frac{1}{2} m_r \dot{x}^2 + \frac{1}{2} \kappa x^2$$

$$E_V = \left(\frac{h}{2\pi}\right) \omega_0 \left(j + \frac{1}{2}\right)$$

$$j = 0,1,2,3\ldots$$

$$\theta_v = \left(\frac{h}{2\pi}\right) \frac{\omega_0}{k} = \left(\frac{h}{2\pi}\right) \frac{1}{k} \sqrt{\frac{\kappa}{m_r}}$$

	$m_r \times 10^{27}\,kg$	$\kappa(N/M)$	$\theta_v\ ^\circ K$
H_2	0.8393	570	6297
N_2	11.629	2240	3354
O_2	13.284	1140	2238
CO	11.392	1860	3087

Note that the vibrational energy is never zero. This zero point energy is actually quite large but it has no effect on the heat capacity and therefore no effect on the temperature of the gas.

$$E_V\big|_{j=0} = \left(\frac{h}{2\pi}\right) \frac{\omega_0}{2}$$

For a monatomic gas there are three translational degrees of freedom. The thermal energy per molecule is

$$\tilde{e} = (3/2)kT$$

where

$$k = 1.38 \times 10^{-23} \, Joules/K.$$

Over one mole of the gas

$$N\tilde{e} = (3/2)R_u T$$

where

$$N = 6.023 \times 10^{26} \ molecules/kmole.$$

The thermal energy per unit mass is

$$e = (3/2)RT$$

For monatomic gases over a very wide range of temperatures

$$C_p = \frac{5}{2}R \quad ; \qquad C_v = \frac{3}{2}R$$

At room temperature a diatomic gas has two additional rotational degrees of freedom.

$$C_p = \frac{7}{2}R \quad ; \qquad C_v = \frac{5}{2}R$$

As the temperature increases two more vibrational degrees of freedom come into play. At very high temperatures

$$C_p = \frac{9}{2}R \quad ; \qquad C_v = \frac{7}{2}R$$

A theory of heat capacity developed using quantum statistical mechanics leads to

$$\frac{C_p}{R} = \frac{7}{2} + \left\{ \frac{(\theta_v/2T)}{Sinh(\theta_v/2T)} \right\}^2$$

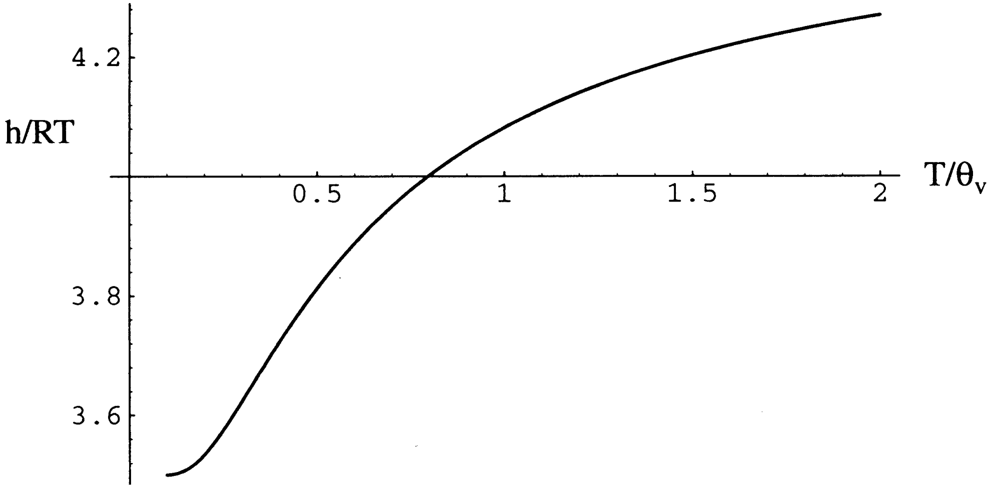
2.11 Enthalpy - diatomic gases

The heat capacity relation can be integrated

$$h(T) = \int C_p dT = R\int\left[\frac{7}{2} + \left\{\frac{(\theta_v/2T)}{Sinh(\theta_v/2T)}\right\}^2\right]dT$$

to give

$$\frac{h(T)}{RT} = \frac{7}{2} + \frac{(\theta_v/T)}{\left(e^{(\theta_v/T)} - 1\right)}$$



Tabulation of enthalpy

Enthalpy per mole of a perfect gas is determined from

$$dh = C_p(T)dT$$

Enthalpy per mole of a perfect gas species i

$$h_i(T) - h_i(T_{ref}) = h_i^\circ(T) - h_i^\circ(T_{ref}) = \int_{Tref}^{T} C_{pi}^\circ(T)dT$$

Standard enthalpy of the ith perfect gas species.

$$h_i^\circ(T_{ref}) = \int_0^{T_{ref}} C_{pi}^\circ dT + h_i^\circ(0)$$

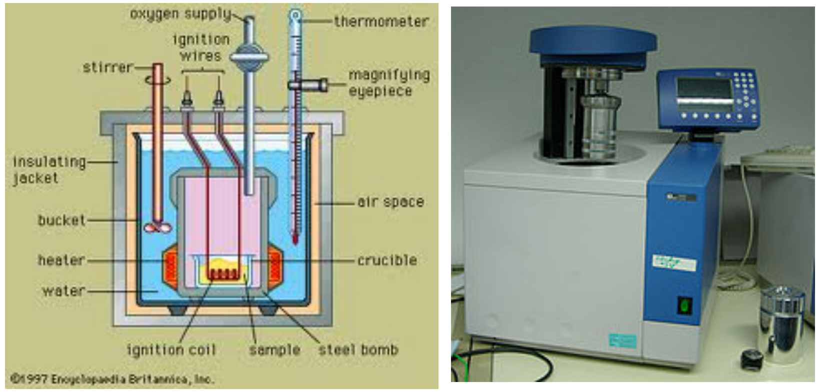
Here the enthalpy constant is the enthalpy change associated with the chemical bond breaking and making at absolute zero.

Actually, it is much easier to use a reference temperature near room temperature.

$$h^{\circ}(T) = \int_{T_{ref}}^{T} C_p^{\circ}(T)\,dT + \Delta h_f^{\circ}\left(T_{ref}\right)$$

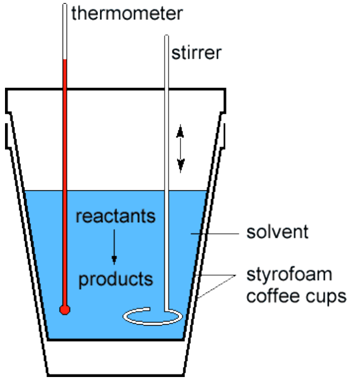
Δh°_{f} is the enthalpy change per mole of a gas species when the atoms are brought together at 298.15K. Most measurements of the chemical bond portion of the enthalpy are made at or close to this temperature.

Bomb Calorimeter

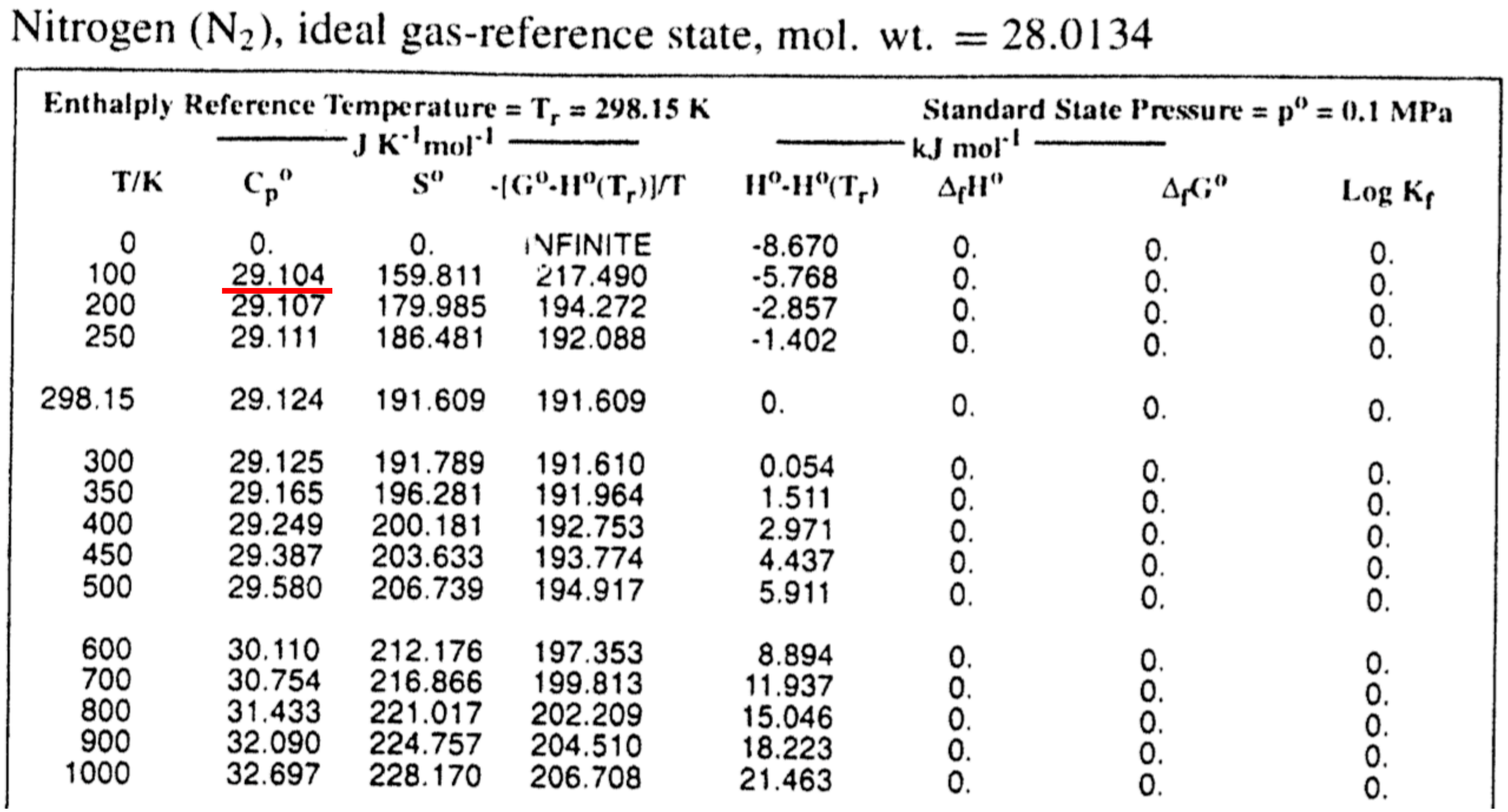


©1997 Encyclopaedia Britannica, Inc.

Coffee cup calorimeter



Tabulated enthalpy for Nitrogen



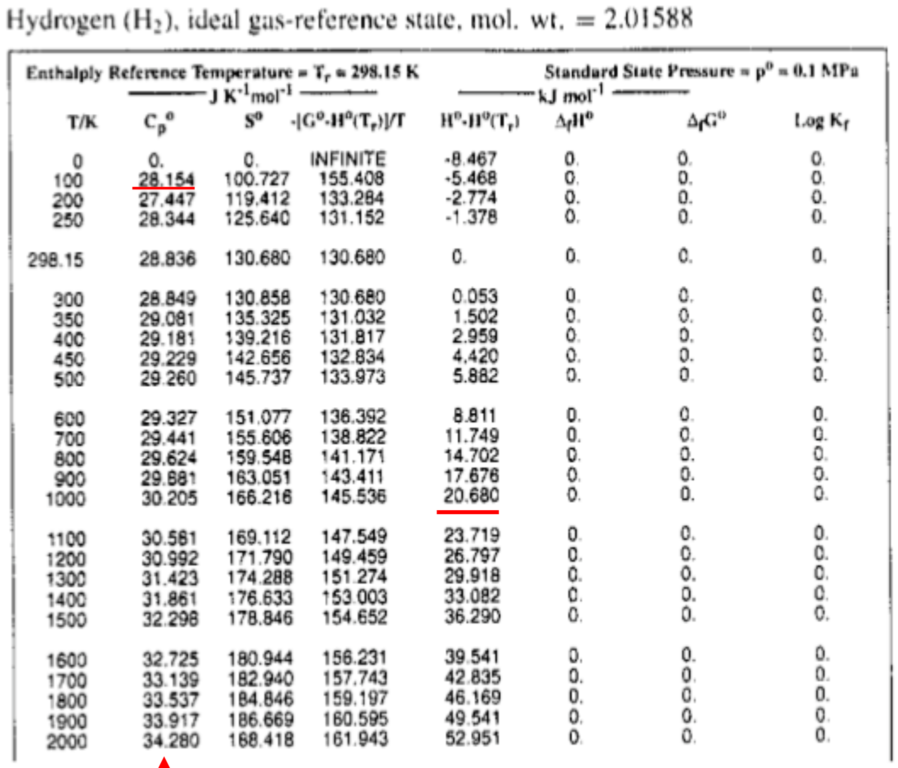
Nitrogen (N_2), ideal gas-reference state, mol. wt. = 28.0134

Enthalpy Reference Temperature = T_r = 298.15 K — Standard State Pressure = p^0 = 0.1 MPa

	J K^{-1}mol^{-1}			kJ mol^{-1}			
T/K	C_p^0	S^0	$-[G^0-H^0(T_r)]/T$	$H^0-H^0(T_r)$	$\Delta_f H^0$	$\Delta_f G^0$	Log K_f
0	0.	0.	INFINITE	-8.670	0.	0.	0.
100	29.104	159.811	217.490	-5.768	0.	0.	0.
200	29.107	179.985	194.272	-2.857	0.	0.	0.
250	29.111	186.481	192.088	-1.402	0.	0.	0.
298.15	29.124	191.609	191.609	0.	0.	0.	0.
300	29.125	191.789	191.610	0.054	0.	0.	0.
350	29.165	196.281	191.964	1.511	0.	0.	0.
400	29.249	200.181	192.753	2.971	0.	0.	0.
450	29.387	203.633	193.774	4.437	0.	0.	0.
500	29.580	206.739	194.917	5.911	0.	0.	0.
600	30.110	212.176	197.353	8.894	0.	0.	0.
700	30.754	216.866	199.813	11.937	0.	0.	0.
800	31.433	221.017	202.209	15.046	0.	0.	0.
900	32.090	224.757	204.510	18.223	0.	0.	0.
1000	32.697	228.170	206.708	21.463	0.	0.	0.

$$\uparrow \sim \frac{7R_u}{2} \qquad R_u = 8.31451\,Joules/gmole-K$$

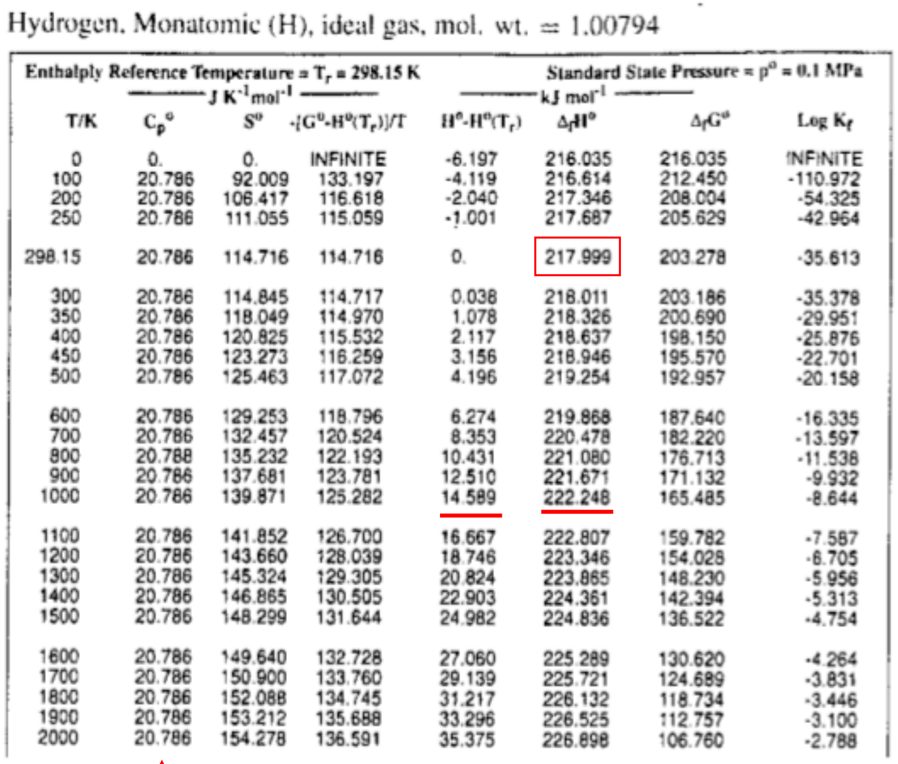
Tabulated enthalpy for Hydrogen



Hydrogen (H_2), ideal gas-reference state, mol. wt. = 2.01588

Enthalpy Reference Temperature = T_r = 298.15 K — **Standard State Pressure = p^0 = 0.1 MPa**

T/K	C_p^0	S^0	$-[G^0-H^0(T_r)]/T$	$H^0-H^0(T_r)$	$\Delta_f H^0$	$\Delta_f G^0$	Log K_f
	$J K^{-1} mol^{-1}$			$kJ\ mol^{-1}$			
0	0.	0.	INFINITE	-8.467	0.	0.	0.
100	28.154	100.727	155.408	-5.468	0.	0.	0.
200	27.447	119.412	133.284	-2.774	0.	0.	0.
250	28.344	125.640	131.152	-1.378	0.	0.	0.
298.15	28.836	130.680	130.680	0.	0.	0.	0.
300	28.849	130.858	130.680	0.053	0.	0.	0.
350	29.081	135.325	131.032	1.502	0.	0.	0.
400	29.181	139.216	131.817	2.959	0.	0.	0.
450	29.229	142.656	132.834	4.420	0.	0.	0.
500	29.260	145.737	133.973	5.882	0.	0.	0.
600	29.327	151.077	136.392	8.811	0.	0.	0.
700	29.441	155.606	138.822	11.749	0.	0.	0.
800	29.624	159.548	141.171	14.702	0.	0.	0.
900	29.881	163.051	143.411	17.676	0.	0.	0.
1000	30.205	166.216	145.536	20.680	0.	0.	0.
1100	30.581	169.112	147.549	23.719	0.	0.	0.
1200	30.992	171.790	149.459	26.797	0.	0.	0.
1300	31.423	174.288	151.274	29.918	0.	0.	0.
1400	31.861	176.633	153.003	33.082	0.	0.	0.
1500	32.298	178.846	154.652	36.290	0.	0.	0.
1600	32.725	180.944	156.231	39.541	0.	0.	0.
1700	33.139	182.940	157.743	42.835	0.	0.	0.
1800	33.537	184.846	159.197	46.169	0.	0.	0.
1900	33.917	186.669	160.595	49.541	0.	0.	0.
2000	34.280	168.418	161.943	52.951	0.	0.	0.



Hydrogen. Monatomic (H), ideal gas, mol. wt. = 1.00794

Enthalpy Reference Temperature = T_r = 298.15 K — **Standard State Pressure = p^0 = 0.1 MPa**

T/K	C_p^0	S^0	$-[G^0-H^0(T_r)]/T$	$H^0-H^0(T_r)$	$\Delta_f H^0$	$\Delta_f G^0$	Log K_f
	$J K^{-1} mol^{-1}$			$kJ\ mol^{-1}$			
0	0.	0.	INFINITE	-6.197	216.035	216.035	INFINITE
100	20.786	92.009	133.197	-4.119	216.614	212.450	-110.972
200	20.786	106.417	116.618	-2.040	217.346	208.004	-54.325
250	20.786	111.055	115.059	-1.001	217.687	205.629	-42.964
298.15	20.786	114.716	114.716	0.	$\boxed{217.999}$	203.278	-35.613
300	20.786	114.845	114.717	0.038	218.011	203.186	-35.378
350	20.786	118.049	114.970	1.078	218.326	200.690	-29.951
400	20.786	120.825	115.532	2.117	218.637	198.150	-25.876
450	20.786	123.273	116.259	3.156	218.946	195.570	-22.701
500	20.786	125.463	117.072	4.196	219.254	192.957	-20.158
600	20.786	129.253	118.796	6.274	219.868	187.640	-16.335
700	20.786	132.457	120.524	8.353	220.478	182.220	-13.597
800	20.788	135.232	122.193	10.431	221.080	176.713	-11.538
900	20.786	137.681	123.781	12.510	221.671	171.132	-9.932
1000	20.786	139.871	125.282	14.589	222.248	165.485	-8.644
1100	20.786	141.852	126.700	16.667	222.807	159.782	-7.587
1200	20.786	143.660	128.039	18.746	223.346	154.028	-6.705
1300	20.786	145.324	129.305	20.824	223.865	148.230	-5.956
1400	20.786	146.865	130.505	22.903	224.361	142.394	-5.313
1500	20.786	148.299	131.644	24.982	224.836	136.522	-4.754
1600	20.786	149.640	132.728	27.060	225.289	130.620	-4.264
1700	20.786	150.900	133.760	29.139	225.721	124.689	-3.831
1800	20.786	152.088	134.745	31.217	226.132	118.734	-3.446
1900	20.786	153.212	135.688	33.296	226.525	112.757	-3.100
2000	20.786	154.278	136.591	35.375	226.898	106.760	-2.788

$\uparrow \sim \frac{7R_u}{2}$

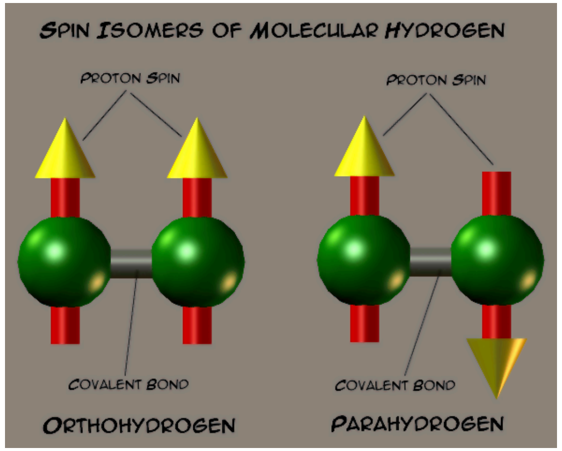
$$R_u = 8.31451 Joules / gmole - K$$

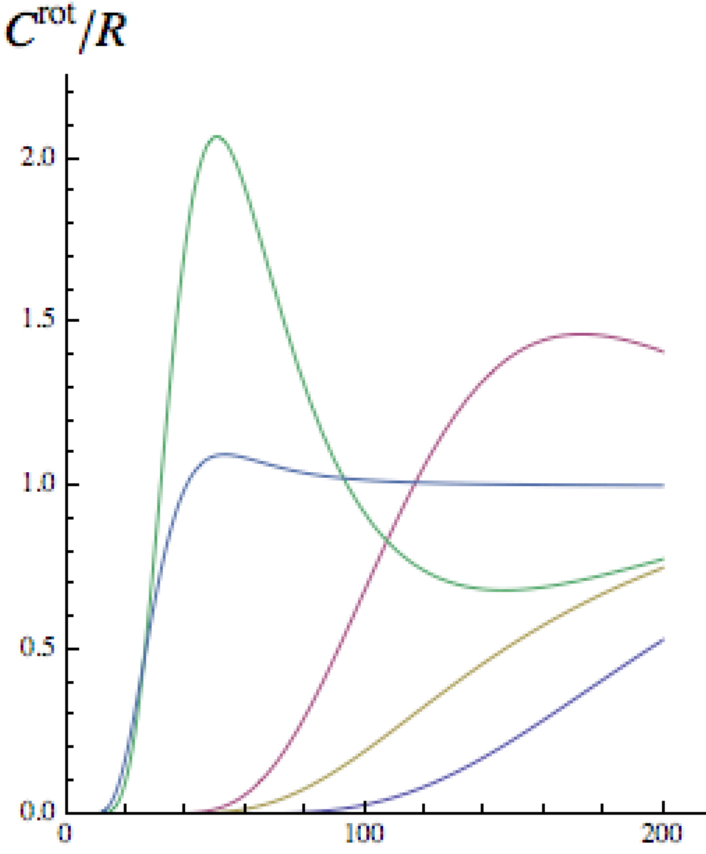
$\uparrow \frac{5R_u}{2}$

Figure A1.1 JANAF data for diatomic and monatomic hydrogen in the temperature range from 0K to 2000K. The full tabulation runs to 6000K.

You can download tabulated data from the NASA Glenn site http://cea.grc.nasa.gov

Hydrogen heat capacity - rotational degrees of freedom





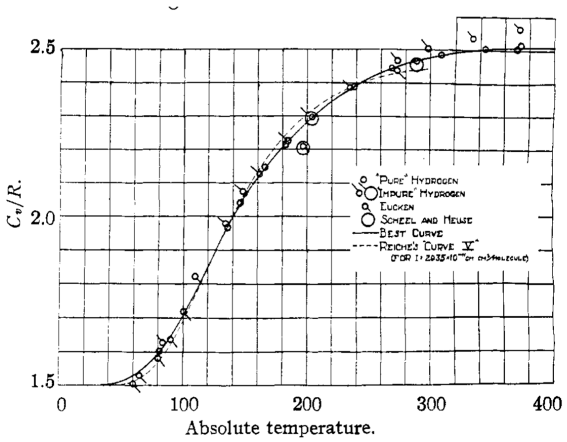
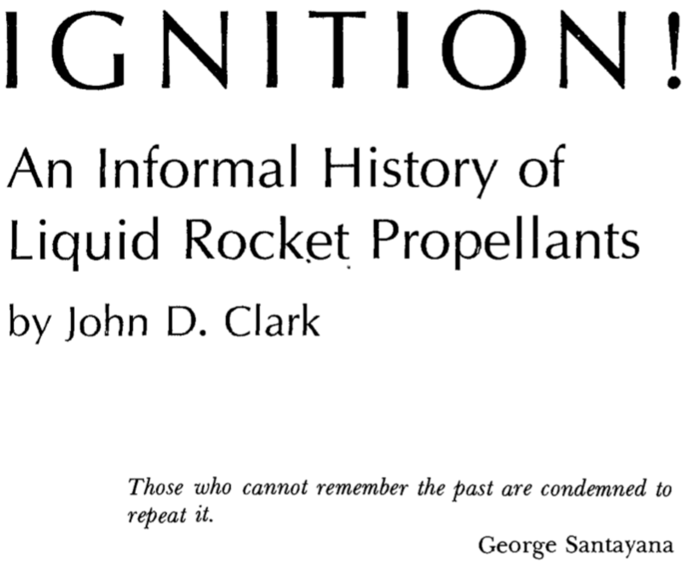


Fig. 3.—Specific heat of hydrogen.

Figure A.13: *From: "The specific heat of hydrogen gas at low temperatures from the velocity of sound", paper by Cornish and Eastman, Journal of the Americal Chemical Society, 1928, 50, 3, 627-652*

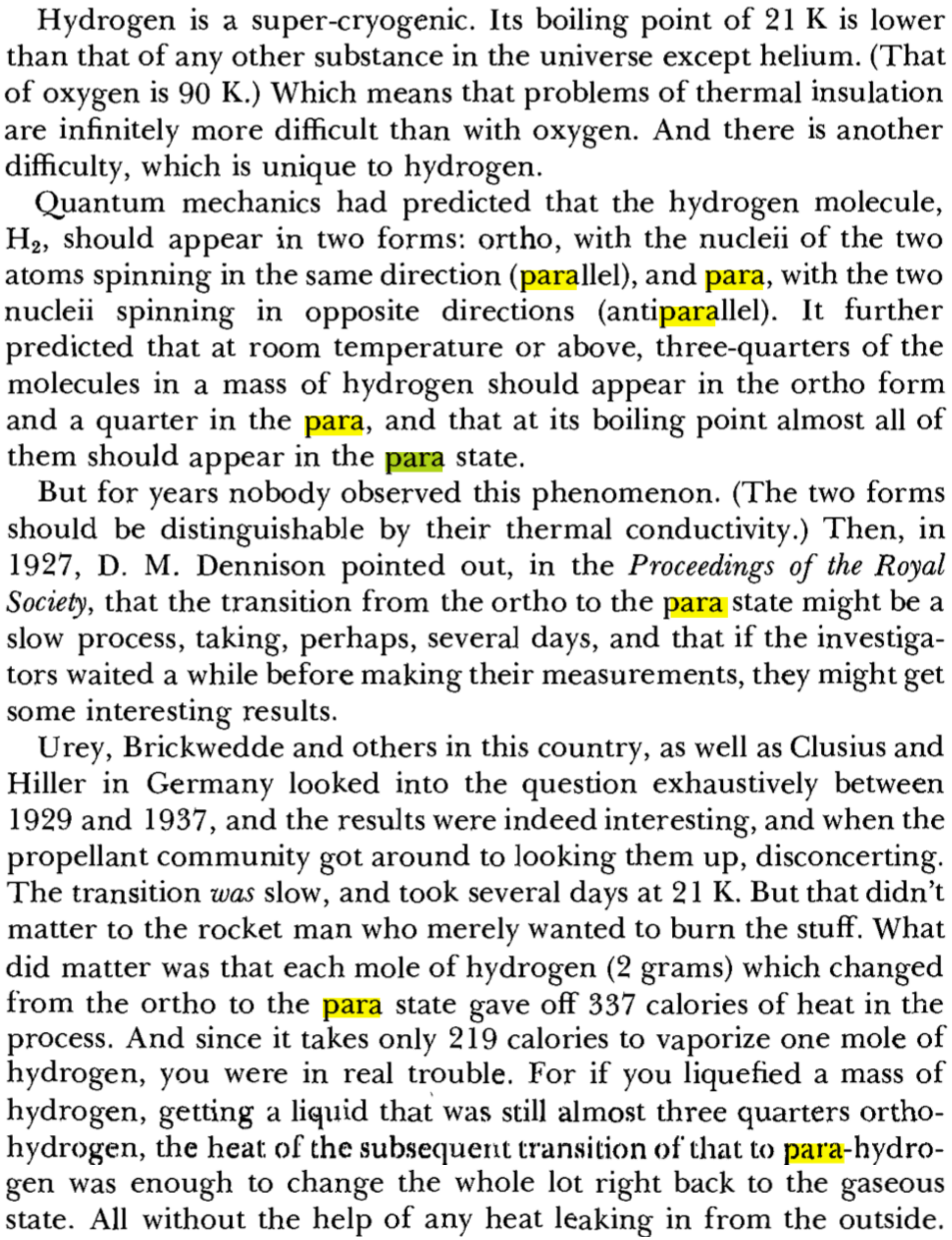


IGNITION!

An Informal History of Liquid Rocket Propellants

by John D. Clark

> *Those who cannot remember the past are condemned to repeat it.*
>
> George Santayana

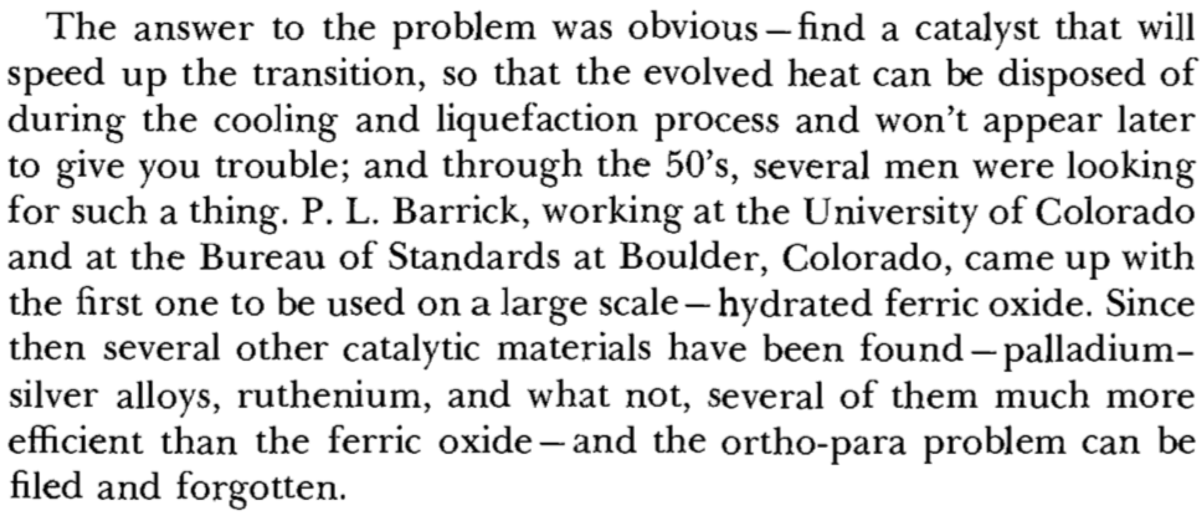


Hydrogen is a super-cryogenic. Its boiling point of 21 K is lower than that of any other substance in the universe except helium. (That of oxygen is 90 K.) Which means that problems of thermal insulation are infinitely more difficult than with oxygen. And there is another difficulty, which is unique to hydrogen.

Quantum mechanics had predicted that the hydrogen molecule, H_2, should appear in two forms: ortho, with the nucleii of the two atoms spinning in the same direction (parallel), and para, with the two nucleii spinning in opposite directions (antiparallel). It further predicted that at room temperature or above, three-quarters of the molecules in a mass of hydrogen should appear in the ortho form and a quarter in the para, and that at its boiling point almost all of them should appear in the para state.

But for years nobody observed this phenomenon. (The two forms should be distinguishable by their thermal conductivity.) Then, in 1927, D. M. Dennison pointed out, in the *Proceedings of the Royal Society*, that the transition from the ortho to the para state might be a slow process, taking, perhaps, several days, and that if the investigators waited a while before making their measurements, they might get some interesting results.

Urey, Brickwedde and others in this country, as well as Clusius and Hiller in Germany looked into the question exhaustively between 1929 and 1937, and the results were indeed interesting, and when the propellant community got around to looking them up, disconcerting. The transition *was* slow, and took several days at 21 K. But that didn't matter to the rocket man who merely wanted to burn the stuff. What did matter was that each mole of hydrogen (2 grams) which changed from the ortho to the para state gave off 337 calories of heat in the process. And since it takes only 219 calories to vaporize one mole of hydrogen, you were in real trouble. For if you liquefied a mass of hydrogen, getting a liquid that was still almost three quarters ortho-hydrogen, the heat of the subsequent transition of that to para-hydrogen was enough to change the whole lot right back to the gaseous state. All without the help of any heat leaking in from the outside.



The answer to the problem was obvious – find a catalyst that will speed up the transition, so that the evolved heat can be disposed of during the cooling and liquefaction process and won't appear later to give you trouble; and through the 50's, several men were looking for such a thing. P. L. Barrick, working at the University of Colorado and at the Bureau of Standards at Boulder, Colorado, came up with the first one to be used on a large scale – hydrated ferric oxide. Since then several other catalytic materials have been found – palladium-silver alloys, ruthenium, and what not, several of them much more efficient than the ferric oxide – and the ortho-para problem can be filed and forgotten.

2.12 Speed of sound

In a homogeneous medium

$$a^2 = \left(\frac{\partial p}{\partial \rho}\right)\bigg|_{s\ =\ constant}$$

For an ideal gas

$$a^2 = \frac{\gamma P}{\rho} = \gamma R T$$

Mach number

$$M = \frac{U}{\sqrt{\gamma R T}}$$

2.13 Atmospheric models

Gravitational potential

$$\nabla P = -\rho \nabla \Psi$$

Near the Earth the gravitational acceleration is nearly constant.

$$\frac{dP}{dz} = -\rho g$$

Constant entropy atmosphere

$$\frac{P}{P_0} = \left(\frac{\rho}{\rho_0}\right)^{\gamma}$$

$$\frac{\rho}{\rho_0} = \left(1 - (\gamma - 1)\frac{gz}{a_0^2}\right)^{\frac{1}{\gamma - 1}}$$

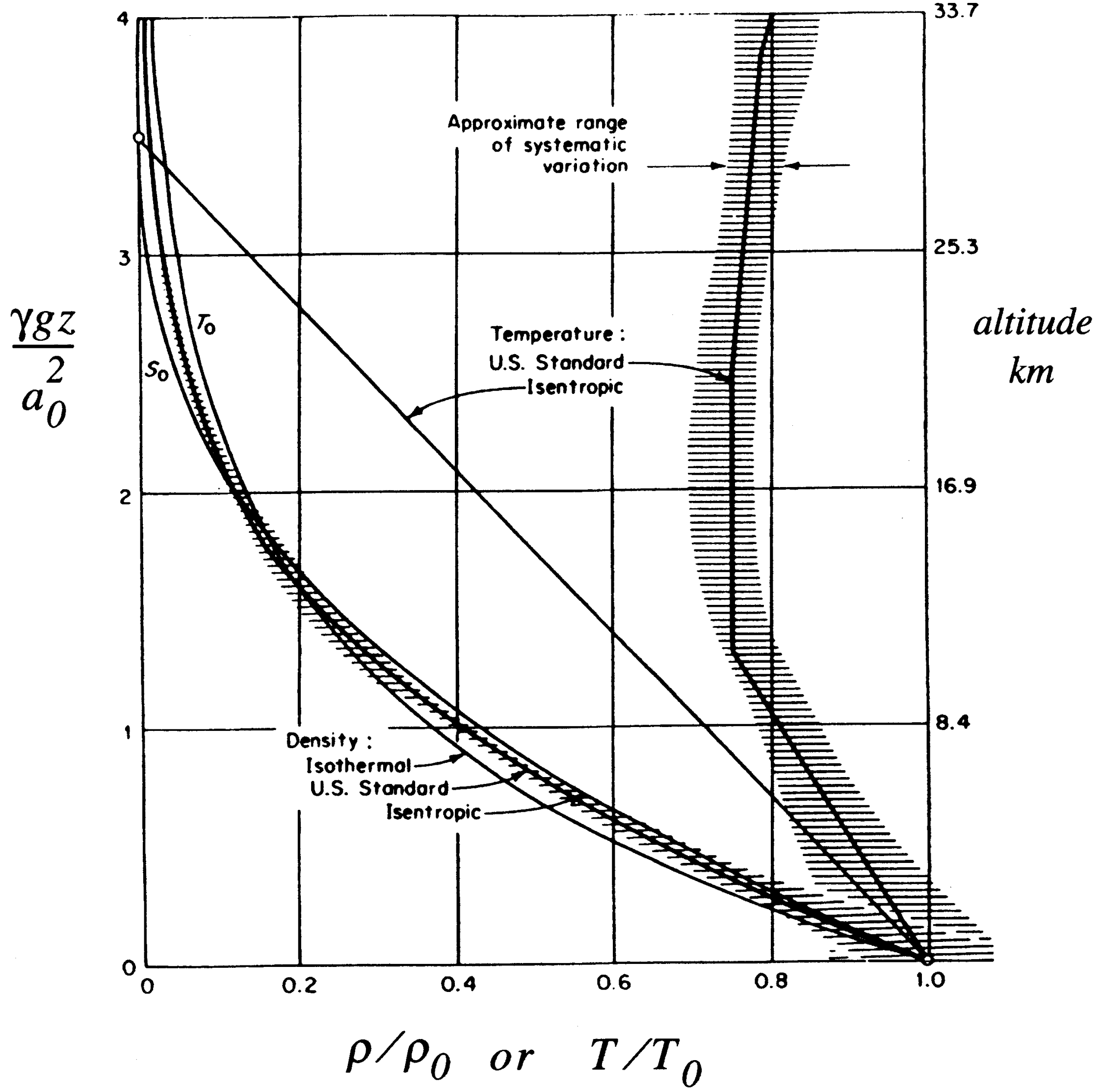
Constant temperature atmosphere

$$\frac{\rho}{\rho_0} = e^{-\frac{\gamma g z}{a_0^2}}$$

Scale height of the atmosphere

$$H = \frac{a_0^2}{\gamma g} = \frac{RT_0}{g}$$

Comparison of atmospheric models



2.14 The Third Law of Thermodynamics

Recall the Gibbs equation written in terms of the enthalpy

$$ds = \frac{dh}{T} - \frac{v}{T}dP$$

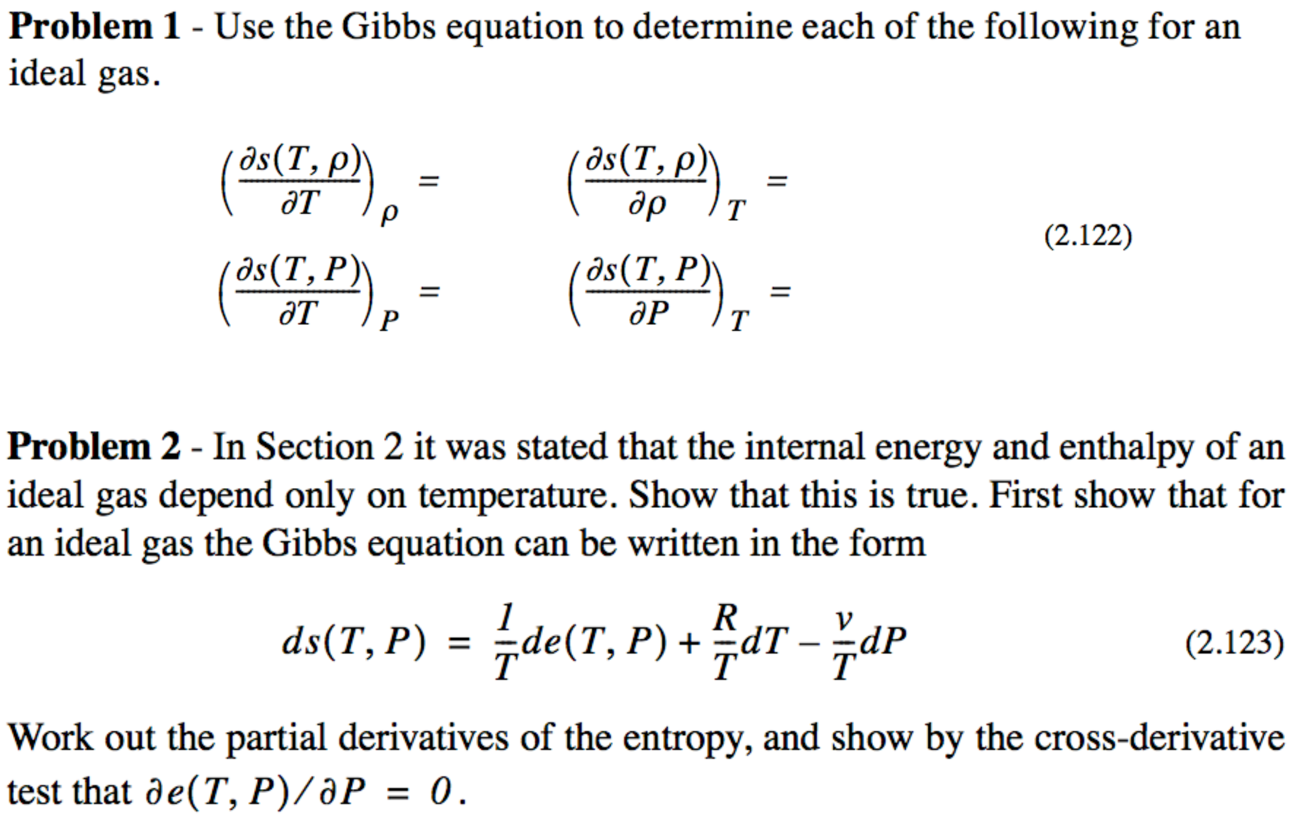
For a process at constant pressure the entropy is

$$S(T) = \int_0^{T_{fusion}} C_p \frac{dT}{T} + \frac{\Delta H_{fusion}}{T_{fusion}} + \int_{T_{fusion}}^{T_{vaporiz}} C_p \frac{dT}{T} + \frac{\Delta H_{vaporiz}}{T_{vaporiz}} + \int_{vaporiz}^{T} C_p \frac{dT}{T}$$

At very low temperatures heat capacity data shows that Cp goes to zero as the temperature goes to zero fast enough so that the first integral converges.

The Third Law states that the entropy of a pure crystalline substance is zero at absolute zero temperature.

2.10 Problems



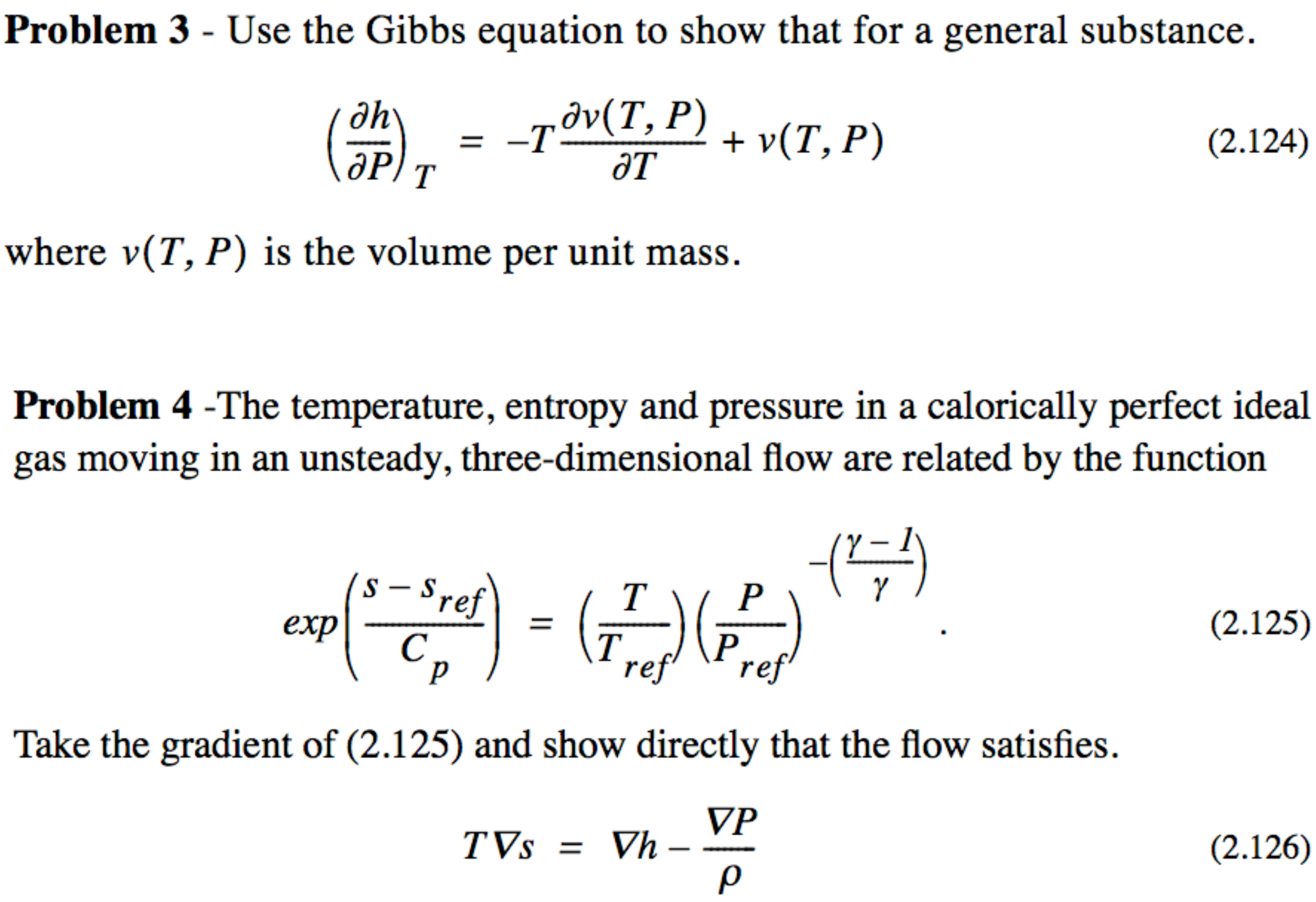
Problem 1 - Use the Gibbs equation to determine each of the following for an ideal gas.

$$\begin{array}{ll} \left(\frac{\partial s(T,\rho)}{\partial T}\right)_{\rho} = & \left(\frac{\partial s(T,\rho)}{\partial \rho}\right)_{T} = \\ \left(\frac{\partial s(T,P)}{\partial T}\right)_{P} = & \left(\frac{\partial s(T,P)}{\partial P}\right)_{T} = \end{array} \tag{2.122}$$

Problem 2 - In Section 2 it was stated that the internal energy and enthalpy of an ideal gas depend only on temperature. Show that this is true. First show that for an ideal gas the Gibbs equation can be written in the form

$$ds(T,P) = \frac{1}{T}de(T,P) + \frac{R}{T}dT - \frac{v}{T}dP \tag{2.123}$$

Work out the partial derivatives of the entropy, and show by the cross-derivative test that $\partial e(T,P)/\partial P = 0$.



Problem 3 - Use the Gibbs equation to show that for a general substance.

$$\left(\frac{\partial h}{\partial P}\right)_T = -T\frac{\partial v(T,P)}{\partial T} + v(T,P) \qquad (2.124)$$

where $v(T,P)$ is the volume per unit mass.

Problem 4 -The temperature, entropy and pressure in a calorically perfect ideal gas moving in an unsteady, three-dimensional flow are related by the function

$$exp\left(\frac{s - s_{ref}}{C_p}\right) = \left(\frac{T}{T_{ref}}\right)\left(\frac{P}{P_{ref}}\right)^{-\left(\frac{\gamma - 1}{\gamma}\right)}. \qquad (2.125)$$

Take the gradient of (2.125) and show directly that the flow satisfies.

$$T\nabla s = \nabla h - \frac{\nabla P}{\rho} \qquad (2.126)$$

Problem 5 - Show that the internal energy of a van der Waals gas is of the form $e(T, v) = f(T) - a/v$.

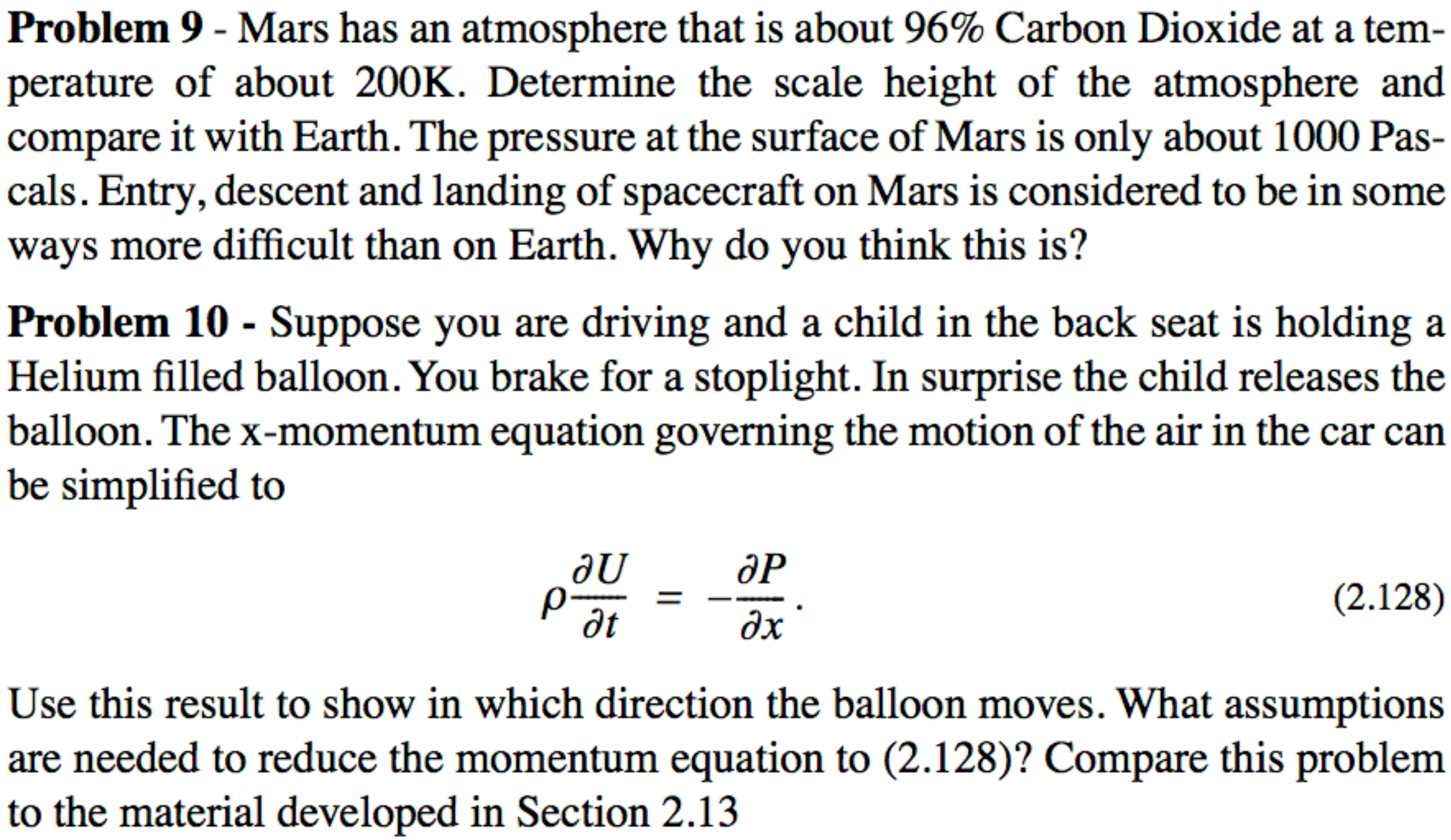
Problem 6 - A heavy piston is dropped from the top of a long, insulated, vertical shaft containing air. The shaft above the piston is open to the atmosphere. Determine the equilibrium height of the piston when it comes to rest. Feel free to introduce whatever data or assumptions you feel are required to solve the problem. Suppose you actually carried out this experiment. How do you think the measured height of the piston would compare with your model?

Problem 7 - In problem 6 what would be the equilibrium height if the gas in the shaft is Helium.

Problem 8 - Consider the nearly isentropic flow of an ideal gas across a low pressure fan such as an aircraft propeller. Assume that the pressure change ΔP is small. Show that the corresponding density change is

$$\frac{\Delta\rho}{\rho_0} \approx \frac{1}{\gamma}\frac{\Delta P}{P_0} \tag{2.127}$$

where ρ_0 and P_0 are the undisturbed values ahead of the fan.



Problem 9 - Mars has an atmosphere that is about 96% Carbon Dioxide at a temperature of about 200K. Determine the scale height of the atmosphere and compare it with Earth. The pressure at the surface of Mars is only about 1000 Pascals. Entry, descent and landing of spacecraft on Mars is considered to be in some ways more difficult than on Earth. Why do you think this is?

Problem 10 - Suppose you are driving and a child in the back seat is holding a Helium filled balloon. You brake for a stoplight. In surprise the child releases the balloon. The x-momentum equation governing the motion of the air in the car can be simplified to

$$\rho\frac{\partial U}{\partial t} = -\frac{\partial P}{\partial x}. \tag{2.128}$$

Use this result to show in which direction the balloon moves. What assumptions are needed to reduce the momentum equation to (2.128)? Compare this problem to the material developed in Section 2.13