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

\[
Td\!s = de + P\!dv
\]

The partial derivatives of the entropy are

\[
\frac{\partial s}{\partial e}\bigg|_v = \text{constant} = \frac{1}{T(e, v)} \quad \frac{\partial s}{\partial v}\bigg|_e = \text{constant} = \frac{P(e, v)}{T(e, v)}.
\]
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

\[
\eta = \frac{\text{work output by the system during the cycle}}{\text{heat added to the system during the cycle}} = \frac{W}{Q_2}
\]

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 \[ \frac{Q_1}{T_1} = \frac{Q_2}{T_2}, \]

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

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

\[
T_{Rankine} = T_{Fahrenheit} + 459.67
\]

\[
T_{Kelvin} = T_{Centigrade} + 273.15.
\]
2.4 Enthalpy

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

\[ h = e + P \nu \]

In terms of the enthalpy, the Gibbs equation becomes

\[ ds = \frac{dh}{T} - \frac{\nu}{T} dP \]

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

\[ ds(h, P) = \frac{dh}{T(h, P)} - \frac{\nu(h, P)}{T(h, P)} dP \]

The partial derivatives of the entropy are

\[ \frac{\partial s}{\partial h} \bigg|_{P = \text{constant}} = \frac{1}{T(h, P)} \quad \frac{\partial s}{\partial P} \bigg|_{h = \text{constant}} = -\frac{\nu(h, P)}{T(h, P)} \]
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.

\[ e = \phi(T, P) ; \quad s = \zeta(T, v) \]
\[ g = \xi(e, P) ; \quad h = \varphi(T, P) \]
\[ s = \theta(h, P) ; \quad s = \beta(e, v) \]
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.

\[ \delta q = de(T,v) + P(T,v)dv = \left( \frac{\partial e}{\partial T} \right)_{v=\text{const}} dT + \left( \frac{\partial e}{\partial v} \right)_{T=\text{const}} dv + P(T,v)dv \]

\[ dv = 0 \]

\[ C_v = \delta q \bigg|_{v=\text{const}} = \left( \frac{\partial e}{\partial T} \right)_{v=\text{const}} \]
Heat capacity at constant pressure.

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

\[ dP = 0 \]

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

\[ h(T, P) = \int C_p(T, P) \, dT + f(P) \]

Typically the heat capacity and enthalpy are tabulated as functions of temperature at a standard pressure of \( 10^5 \text{ N/}m^2 \).

The standard enthalpy of a substance at temperature \( T \) is.

\[ h^\circ(T) = \int_{0}^{T_{\text{fusion}}} C_p^\circ(T) \, dT + \Delta H_{\text{fusion}}^\circ + \int_{T_{\text{fusion}}}^{T_{\text{vaporization}}} C_p^\circ(T) \, dT + \Delta H_{\text{vaporization}}^\circ + \int_{T_{\text{vaporization}}}^{T} C_p^\circ(T) \, dT \]
2.6 Ideal gases (also called perfect gases)

Ideal (perfect) gas equation of state

\[ P = \frac{nR_u T}{V} \]

Universal gas constant

\[ R_u = 8314.510 \text{ Joules/(kmole} - K) \]

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

\[ P = \rho RT \]
where

\[ R = \frac{R_u}{M_w} \]

For Air the gas constant is

\[ M_w \bigg|_{air} = 28.9644 \text{ kilograms/kmole} \]

\[ R = 287.06 \text{ m}^2/\text{sec}^2 - K \]

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

\[ de = C_v(T) dT \quad ; \quad dh = C_p(T) dT \]

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.

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

\[
\frac{a}{b} = \frac{27}{8} R T_c , \quad \frac{a}{b^2} = 27 P_c
\]
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

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

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

\[ \frac{P_2}{P_1} \]

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

Thermal energy

\[ E - E_{\text{ref}} = m_a C_v (T_a - T_{\text{ref}}) + m_b C_v (T_b - T_{\text{ref}}) = (m_a + m_b) C_v (T_{\text{final}} - T_{\text{ref}}) \]

\[ m_a C_v T_a + m_b C_v T_b = (m_a + m_b) C_v T_{\text{final}} \]
From the ideal gas law

\[ PV = m_a RT_a = m_b RT_b \]

\[ \frac{m_b}{m_a} = \frac{T_a}{T_b} \]

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

For a constant pressure process

\[
\frac{s_{\text{final}} - s_a}{C_p} = \ln \frac{T_{\text{final}}}{T_a}
\]

\[
\frac{s_{\text{final}} - s_b}{C_p} = \ln \frac{T_{\text{final}}}{T_b}
\]
Entropy change of the system

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

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

\[
\frac{s_{\text{final}} - s_{\text{initial}}}{C_p} = -0.405465 + 2(0.28768) = 0.0566
\]
2.8.2 

Entropy change due to mixing of distinct gases

Intensive entropy of each gas

\[
ds_a = \int C_p \frac{dT}{T} - R \frac{dP}{P} \frac{R_u}{M_{w_a}} \ln P + \alpha_a
\]

\[
ds_b = \int C_p \frac{dT}{T} - R \frac{dP}{P} \frac{R_u}{M_{w_b}} \ln P + \alpha_b
\]

Extensive entropy of the system

\[
S = m_a s_a + m_b s_b
\]
Define mass fractions

\[
\chi_a = \frac{m_a}{m_a + m_b} \quad \chi_b = \frac{m_b}{m_a + m_b}
\]

Intensive entropy of the system before mixing

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

\[
s_{before} = \chi_a \left( \int C_{p_a} \frac{dT}{T} - \frac{R_u}{M_{w_a}} \ln P + \alpha_a \right) + \chi_b \left( \int C_{p_b} \frac{dT}{T} - \frac{R_u}{M_{w_b}} \ln P + \alpha_b \right)
\]
After mixing each gas fills the volume. Partial pressures after mixing are

\[ P_a = \frac{m_a}{V} \frac{R_u}{M_{w_a}} T \quad \quad P_b = \frac{m_b}{V} \frac{R_u}{M_{w_b}} T \]

\[ P = P_a + P_b \]

\[ s_{after} = \chi_a \left( \int C_p \frac{dT}{T} - \frac{R_u}{M_{w_a}} \ln P_a + \alpha_a \right) + \chi_b \left( \int C_p \frac{dT}{T} - \frac{R_u}{M_{w_b}} \ln P_b + \alpha_b \right) \]

\[ s_{after} - s_{before} = \chi_a \frac{R_u}{M_{w_a}} \ln \left( \frac{P}{P_a} \right) + \chi_b \frac{R_u}{M_{w_b}} \ln \left( \frac{P}{P_b} \right) > 0 \]
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

\[
\frac{T_f}{T_i} = \left( \frac{P_a}{P_i} \right)^{\frac{\gamma - 1}{\gamma}}
\]  

(2.82)

Entropy change for the ejected gas

\[
\frac{s_f - s_i}{C_p} = \log \left( \frac{T_a}{T_i} \right) - \left( \frac{\gamma - 1}{\gamma} \right) \log \left( \frac{P_a}{P_i} \right)
\]  

(2.83)
2.9.2 Work done by an expanding gas

![Diagram of gas expansion](image)

Figure 2.12 Projectile energized by an expanding gas

\[
W = \int_{L_1}^{L_2} \frac{P}{m} dV = \frac{1}{2} m U_2^2
\] (2.84)

\[
\frac{P}{P_1} = \left( \frac{\rho}{\rho_1} \right) \gamma = \left( \frac{4m_{\text{gas}}}{\frac{\pi d^2 L}{4m_{\text{gas}}}} \right)^\gamma = \left( \frac{L_1}{L} \right) \gamma
\] (2.85)
\[ \frac{1}{2} m U_2^2 = \left( \frac{\pi d^2}{4} \right) \int_{L_1}^{L_2} P_1 \left( \frac{L_1}{L} \right) \gamma \, dL. \] (2.86)

\[ \frac{1}{2} m U_2^2 = \left( \frac{\pi d^2}{4} \right) \frac{P_1 L_1^\gamma}{1-\gamma} \left( L_2^{1-\gamma} - L_1^{1-\gamma} \right) \] (2.87)

\[ \frac{1}{2} m U_2^2 = \left( \frac{\pi d^2 L_1}{4} \right) \frac{P_1}{\gamma-1} \left( 1 - \left( \frac{L_1}{L_2} \right)^{\gamma-1} \right) \] (2.88)

\[ V_1 = \frac{\pi d^2 L_1}{4}. \] (2.89)

\[ \frac{1}{2} m U_2^2 = \frac{P_1 V_1}{\gamma-1} \left( 1 - \left( \frac{L_1}{L_2} \right)^{\gamma-1} \right) \] (2.90)

\[ \frac{1}{2} m U_2^2 = m_{gas} C_v T_1 \left( 1 - \left( \frac{L_1}{L_2} \right)^{\gamma-1} \right) \] (2.91)
2.9.3 Example - Helium gas gun

Figure 2.12 Projectile energized by an expanding gas

\[ P_1 = 4 \times 10^8 \text{ N/M}^2 \quad T_1 = 2000^\circ K \quad L_2 = 2 \text{ M} \]
\[ d = 0.04 \text{ M} \quad m = 0.1 \text{ kg} \quad M_w = 4.0026 \]

\[ P_1 V_1 = m_{\text{gas}} \left( \frac{R_u}{M_w} \right) T_1. \]  \hspace{1cm} (2.92)

\[ m_{\text{gas}} = \frac{P_1 V_1 \left( \frac{M_w}{R_u} \right)}{T_1} = \frac{4 \times 10^8}{2000} \left( \frac{\pi(0.04)^2(0.1)}{4} \right) \left( \frac{4.0026}{8314.472} \right) = 0.01208 \text{ Kg} \]  \hspace{1cm} (2.93)
\[ C_v = (3/2)R \]

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

(2.94)

\[ a_1 = \sqrt{\gamma RT_1} = 2631 \text{ M/Sec.} \]  

(2.95)

\[ T_2 = T_1 \left( \frac{L_1}{L_2} \right)^{\gamma - 1} = 2000 \left( \frac{0.1}{2} \right)^{2/3} = 271 \text{ K.} \]  

(2.96)

\[ a_2 = \sqrt{\gamma RT_2} = 968 \text{ M / Sec} \]  

(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.

\[ C_p = \frac{\beta + 2}{2} R \; ; \quad C_v = \frac{\beta}{2} R \; ; \quad \gamma = \frac{\beta + 2}{\beta} \]

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.

\[ k = 1.38 \times 10^{-23} \text{ Joules/K} \]
Molecular model of a gas

monatomic gas

\[ E = \frac{1}{2} m u^2 + \frac{1}{2} m v^2 + \frac{1}{2} m w^2 \]

diatomic gas

\[ E_{\text{solid dumbbell}} = \frac{1}{2} I_1 \omega_1^2 + \frac{1}{2} I_2 \omega_2^2 + \frac{1}{2} I_3 \omega_3^2 \]

spring-mass

\[ E_{\text{spring-mass}} = \frac{1}{2} m_r \dot{x}^2 + \frac{1}{2} \kappa x^2 \]
diatomic gas

\[ E_{\text{solid dumbbell}} = \frac{1}{2} I_1 \omega_1^2 + \frac{1}{2} I_2 \omega_2^2 + \frac{1}{2} I_3 \omega_3^2 \]

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

\[ K = 0, 1, 2, 3, \ldots \]

\[ E_{2, \text{diatomic molecule}} = \left( \frac{h}{2\pi} \right)^2 \frac{K(K+1)}{2I_{2, 3}} = \left( \frac{h}{2\pi} \right)^2 \frac{K(K+1)}{2(m_rD^2)} \]

\[ \frac{1}{2} k \theta_r \approx E_{2, \text{diatomic molecule}} \]

\[ \theta_r = \left( \frac{h}{2\pi} \right)^2 \frac{1}{2k(m_rD^2)} \]

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

\[ \theta_{r1} = \left( \frac{h}{2\pi} \right)^2 \frac{1}{2kI_1} \]

\[ \theta_{r1, \text{electron cloud hollow sphere}} \approx 3670 \theta_r \]
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.

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

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

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

<table>
<thead>
<tr>
<th></th>
<th>$m_r \times 10^{27}$ kg</th>
<th>$\kappa (N/M)$</th>
<th>$\theta_v , ^\circ K$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$</td>
<td>0.8393</td>
<td>570</td>
<td>6297</td>
</tr>
<tr>
<td>N$_2$</td>
<td>11.629</td>
<td>2240</td>
<td>3354</td>
</tr>
<tr>
<td>O$_2$</td>
<td>13.284</td>
<td>1140</td>
<td>2238</td>
</tr>
<tr>
<td>CO</td>
<td>11.392</td>
<td>1860</td>
<td>3087</td>
</tr>
</tbody>
</table>

$$E_V\big|_{j=0} = \left( \frac{h}{2\pi} \right) \frac{\omega_0}{2}$$
For a monatomic gas there are three translational degrees of freedom. The thermal energy per molecule is

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

where

\[ k = 1.38 \times 10^{-23} \text{ Joules/K}. \]

Over one mole of the gas

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

where

\[ N = 6.023 \times 10^{26} \text{ molecules/kmole}. \]
The thermal energy per unit mass is

\[ e = \left( \frac{3}{2} \right) RT \]

For monatomic gases over a very wide range of temperatures

\[ C_p = \frac{5}{2} R ; \quad C_v = \frac{3}{2} R \]

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

\[ C_p = \frac{7}{2} R ; \quad C_v = \frac{5}{2} R \]
As the temperature increases two more vibrational degrees of freedom come into play. At very high temperatures,

\[
C_p = \frac{9}{2} R \quad ; \quad C_v = \frac{7}{2} R
\]

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

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

to give

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

\[ h_i(T) - h_i(T_{\text{ref}}) = h_i^o(T) - h_i^o(T_{\text{ref}}) = \int_{T_{\text{ref}}}^{T} C_{pi}^o(T)\,dT \]

Standard enthalpy of the ith perfect gas species.

\[ h_i^o(T_{\text{ref}}) = \int_{0}^{T_{\text{ref}}} C_{pi}^o\,dT + h_i^o(0) \]

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.

\[
\Delta h^\circ (T) = \int_{T_{\text{ref}}}^{T} C_p^\circ (T) \, dT + \Delta h_f^\circ (T_{\text{ref}})
\]

\(\Delta h_f^\circ\) 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.
Tabulated enthalpy for Nitrogen

Nitrogen (N₂), ideal gas-reference state, mol. wt. = 28.0134

<table>
<thead>
<tr>
<th>T/K</th>
<th>C_p⁰</th>
<th>S⁰</th>
<th>-(G⁰-H⁰(T))/T</th>
<th>H⁰-H⁰(T_r)</th>
<th>ΔfH⁰</th>
<th>ΔfG⁰</th>
<th>Log K_f</th>
</tr>
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<tr>
<td>0</td>
<td>0.</td>
<td>0.</td>
<td>INFINITE</td>
<td>-8.670</td>
<td>0.</td>
<td>0.</td>
<td>0.</td>
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<tr>
<td>100</td>
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<tr>
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<td>191.610</td>
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<td>197.353</td>
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<td>199.813</td>
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<td>221.017</td>
<td>202.209</td>
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</tr>
<tr>
<td>1000</td>
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<td>206.708</td>
<td>21.463</td>
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<td>0.</td>
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</tr>
</tbody>
</table>

\[ \sim \frac{7R_u}{2} \quad R_u = 8.31451 \text{Joules} / \text{gmole} - K \]
Tabulated enthalpy for Hydrogen

Hydrogen (H₂), ideal gas-reference state, mol. wt. = 2.01588

<table>
<thead>
<tr>
<th>Enthalpy Reference Temperature (T, K)</th>
<th>Standard State Pressure (p₀ = 0.1 MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T/K</td>
<td>C_p^0 (J K⁻¹ mol⁻¹)</td>
</tr>
<tr>
<td>--------------------------------------</td>
<td>----------------------</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>100</td>
<td>0.15</td>
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<tr>
<td>200</td>
<td>0.24</td>
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<tr>
<td>250</td>
<td>0.29</td>
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</table>

<table>
<thead>
<tr>
<th>Enthalpy Reference Temperature (T, K)</th>
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<td>T/K</td>
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</tr>
<tr>
<td>298.15</td>
<td>0.29</td>
</tr>
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<td>300</td>
<td>0.29</td>
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<tr>
<td>350</td>
<td>0.29</td>
</tr>
<tr>
<td>400</td>
<td>0.29</td>
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<td>450</td>
<td>0.29</td>
</tr>
<tr>
<td>500</td>
<td>0.29</td>
</tr>
</tbody>
</table>

\[ R_u \approx \frac{7R_u}{2} \]

\[ R_u = 8.31451 \text{Joules / gmole} - \text{K} \]

\[ \frac{5R_u}{2} \]

**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

\[ C^{\text{rot}}/R \]

- para \( H_2 \)
- HD
- equilibrium \( H_2 \)
- 3:1 mixture
- ortho \( H_2 \)
2.12 Speed of sound

In a homogeneous medium

\[ a^2 = \left( \frac{\partial p}{\partial \rho} \right)_s = \text{constant} \]

For an ideal gas

\[ a^2 = \frac{\gamma p}{\rho} = \gamma RT \]

Mach number

\[ M = \frac{U}{\sqrt{\gamma RT}} \]
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

\[ \frac{\rho}{\rho_0} = e^{\frac{\gamma gz}{a_0^2}} \]

Scale height of the atmosphere

\[ H = \frac{a_0^2}{\gamma g} = \frac{RT_0}{g} \]
Comparison of atmospheric models

\[ \frac{\gamma g z}{2 a_0} \]

\[ \rho / \rho_0 \text{ or } T / T_0 \]

Temperature:
- U.S. Standard Isentropic

Density:
- Isothermal
- U.S. Standard Isentropic

Approximate range of systematic variation

altitude

km
2.14 The Third Law of Thermodynamics

Recall the Gibbs equation written in terms of the enthalpy

\[ ds = \frac{dh}{T} - \frac{\nu}{T}dP \]

For a process at constant pressure the entropy is

\[ S(T) = \int_{T_{\text{fusion}}}^{T} C_p \frac{dT}{T} + \frac{\Delta H_{\text{fusion}}}{T_{\text{fusion}}} + \int_{T_{\text{fusion}}}^{T_{\text{vaporiz}}} C_p \frac{dT}{T} + \frac{\Delta H_{\text{vaporiz}}}{T_{\text{vaporiz}}} + \int_{T_{\text{vaporiz}}}^{T} C_p \frac{dT}{T} \]

At very low temperatures heat capacity data shows that \( C_p \) 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.

\[
\left( \frac{\partial s(T, \rho)}{\partial T} \right)_\rho = \left( \frac{\partial s(T, \rho)}{\partial \rho} \right)_T =
\]

\[
\left( \frac{\partial s(T, P)}{\partial T} \right)_P = \left( \frac{\partial s(T, P)}{\partial P} \right)_T =
\]  \hspace{1cm} (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

\[
ds(T, P) = \frac{1}{T} de(T, P) + \frac{R}{T} dT - \frac{\nu}{T} dP
\]  \hspace{1cm} (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.

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

(2.124)

where \( \nu(T, P) \) 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

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

(2.125)

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

$$T \nabla s = \nabla h - \frac{\nabla P}{\rho}$$

(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 \( \Delta P \) is small. Show that the corresponding density change is
\[
\frac{\Delta \rho}{\rho_0} \approx \frac{1}{\gamma} \frac{\Delta P}{P_0}
\]

where \( \rho_0 \) 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

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

(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
**Problem** – In the figure below one mole of nitrogen is contained in Volume A at State 1. Volume B is at vacuum. A small leak is opened between Volumes A and B. The gas in A expands slowly while the jet of gas from the leak fills B until the pressures in Volume A and B are equal. At that point the leak is sealed. The volumes and the wall between them are adiabatic. The two volumes are equal.

State 1

- \( P_{A_1} = 10^6 \, \text{N/m}^2 \)
- \( T_{A_1} = 600 \, \text{K} \)
- \( n_{A_1} = 1 \, \text{mole} \)

\( V_A = V_B \)

State 2

- \( P_{A_2} = \? \, \text{N/m}^2 \)
- \( T_{A_2} = \? \, \text{K} \)
- \( n_{A_2} = \? \, \text{mole} \)

- \( P_{B_2} = \? \, \text{N/m}^2 \)
- \( T_{B_2} = \? \, \text{K} \)
- \( n_{B_2} = \? \, \text{mole} \)

\( V_A = V_B \)

\( P_{A_2} = P_{B_2} \)

1) Use the first law of thermodynamics to relate the internal energy of the gas in Volume A at State \( A_1 \) to the gases in A at State \( A_2 \) and B at State \( B_2 \).

2) Relate the pressures and temperatures in Volume A at States 1 and 2.

3) Determine \( T_{A_2} \), \( T_{B_2} \), \( n_{A_2} \), \( n_{B_2} \) and \( P_{A_2} \).

4) Determine the dimensionless entropy change of the system \( \Delta S / (nC_p) \) where \( n \) is the number of moles of gas in the system. Note that \( C_p \) is the molar heat capacity.
Low-Temperature Heat Capacity of Hydrogen Molecules

Hydrogen $\text{H}_2$ is the lowest boiling molecular species, remaining a gas down to 20K. At and above room temperature, $T \gtrsim 300$ K, the rotational degree of freedom is fully excited; thus the rotational contribution to heat capacity approaches its equipartition value, $\frac{1}{2} g$ per mole. Owing to the exceptionally small moment of inertia of $\text{H}_2$, rotation becomes inactive at temperatures below about 50K. However, the heat capacity behaves anomalously as the temperature is lowered. This anomaly was first explained by Dennison in 1927. Since $\text{H}_2$ is a homonuclear molecule, only half of its rotational states are accessible. In the singlet nuclear-spin state, known as parahydrogen ($\text{p-H}_2$), only even-$J$ rotational states are accessible; in the triplet nuclear-spin state, known as orthohydrogen ($\text{o-H}_2$), only odd-$J$ rotational states are accessible. The molecular partition functions representing the rotational and nuclear spin degrees of freedom are given by

$$q_{\text{ortho}} = \sum_{J=0}^{\infty} (2J+1) e^{-\frac{J(J+1)\hbar^2}{2kT}},$$

$$q_{\text{para}} = \sum_{J=1}^{\infty} (2J+1) e^{-\frac{J(J+1)\hbar^2}{2kT}}.$$

The rotational energies are given by $E_J = J(J+1)\hbar^2/2I$ with $(2J+1)$-fold degeneracies. It is convenient to define the rotational characteristic function $\Theta = \hbar^2/2Ik$, equal to 87.57 for [more]
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?
Model 1 - Adiabatic, *isentropic* compression. In this case it is assumed that there is sufficient friction between the piston and the wall to insure that the piston drops very slowly. All piston potential energy is dissipated by the wall friction and viscous friction within the gas is small.

\[
\alpha = \frac{m_{\text{piston}} g}{P_1 A} > 1
\]

\[
m_{\text{gas}} = \frac{P_1 A h_1}{R T_1} = \frac{P_2 A h_2}{R T_2}
\]

\[
\frac{P_1 h_1}{T_1} = \frac{P_2 h_2}{T_2}
\]

\[
P_2 = P_1 + \frac{m_{\text{piston}} g}{A}
\]

\[
\lim_{\alpha \to 0} \frac{T_2}{T_1} = 1 + \frac{\gamma - 1}{\gamma} \alpha
\]

\[
\lim_{\alpha \to 0} \frac{h_2}{h_1} = 1 - \frac{1}{\gamma} \alpha
\]

Isentropic relations

\[
\frac{h_1}{h_2} = \left( \frac{T_2}{T_1} \right)^{\gamma - 1} = \left( \frac{P_2}{P_1} \right)^{\frac{1}{\gamma}} = \left( \frac{P_1 A + m_{\text{piston}} g}{P_1 A} \right)^{\frac{1}{\gamma}}
\]

\[
\frac{T_2}{T_1} = (1 + \alpha)^{\frac{\gamma - 1}{\gamma}}
\]

\[
\frac{h_2}{h_1} = \left( \frac{1}{1 + \alpha} \right)^{\frac{1}{\gamma}}
\]
Model 2 - Adiabatic non-isentropic compression. In this case there is no friction between the wall and the piston but there is viscous friction within the gas. All piston potential energy is converted to gas internal energy.

\[ \alpha = \frac{m_{\text{piston}} g}{P_1 A} > 1 \]

\[ m_{\text{gas}} = \frac{P_1 A h_1}{RT_1} = \frac{P_2 A h_2}{RT_2} \]

\[ \frac{P_1 h_1}{T_1} = \frac{P_2 h_2}{T_2} \]

\[ P_2 = P_1 + \frac{m_{\text{piston}} g}{A} \]

Energy balance

\[ m_{\text{piston}} g (h_1 - h_2) + P_1 A (h_1 - h_2) = m_{\text{gas}} C_v (T_2 - T_1) \]

\[ \left( m_{\text{piston}} g h_1 + P_1 A h_1 \right) \left( 1 - \frac{h_2}{h_1} \right) = m_{\text{gas}} C_v T_1 \left( \frac{T_2}{T_1} - 1 \right) \]

\[ \frac{h_2}{h_1} = \frac{T_2}{T_1} \frac{P_1}{P_2} \left( \frac{P_1 A}{P_1 A + m_{\text{piston}} g} \right) = \frac{T_2}{T_1} \left( \frac{1}{1 + \frac{m_{\text{piston}} g}{P_1 A}} \right) = \frac{T_2}{T_1} \left( \frac{1}{1 + \alpha} \right) \]
\[
\left(1 - \frac{T_2}{T_1}\left(1 + \frac{m_{\text{piston}} g}{P_1 A}\right)\right) = \frac{m_{\text{gas}} C_v T_1}{m_{\text{piston}} g h_1 + P_1 A h_1} \frac{T_2}{T_1} - 1
\]

\[
m_{\text{gas}} = \frac{P_1 A h_1}{RT_1} = \frac{P_2 A h_2}{RT_2}
\]

\[
\left(1 - \frac{T_2}{T_1}\left(1 + \frac{m_{\text{piston}} g}{P_1 A}\right)\right) = \frac{1}{(\gamma - 1)} \frac{P_1 A}{m_{\text{piston}} g + P_1 A} \frac{T_2}{T_1} - 1
\]

\[
\alpha = \frac{m_{\text{piston}} g}{P_1 A} > 1
\]

\[
\left(1 - \frac{T_2}{T_1}\left(1 + \alpha\right)\right) = \frac{1}{(\gamma - 1)} \frac{1}{(1 + \alpha)} \frac{T_2}{T_1} - 1
\]

\[
\frac{T_2}{T_1} = \left(\frac{\gamma - 1}{\gamma}\right)(1 + \alpha) + \frac{1}{\gamma} = 1 + \left(\frac{\gamma - 1}{\gamma}\right)\alpha
\]

\[
\frac{\gamma - 1}{\gamma} \alpha
\]

\[
\lim_{\alpha \to \infty} \frac{h_2}{h_1} = \frac{\gamma - 1}{\gamma}
\]

\[
\lim_{\alpha \to 0} \frac{h_2}{h_1} = 1 - \frac{1}{\gamma} \alpha
\]

\[
\frac{T_2}{T_1} = 1 + \frac{\gamma - 1}{\gamma} \alpha
\]

\[
\frac{h_2}{h_1} = \frac{1 + \frac{\gamma - 1}{\gamma} \alpha}{1 + \alpha}
\]
\[
\frac{T_2}{T_1} = 1 + \frac{\gamma - 1}{\gamma} \alpha \quad \text{adiabatic, non-isentropic}
\]

\[
\frac{T_2}{T_1} = (1 + \alpha)^{\frac{\gamma - 1}{\gamma}} \quad \text{adiabatic, isentropic}
\]

\[
\frac{h_2}{h_1} = \frac{1 + \frac{\gamma - 1}{\gamma} \alpha}{1 + \alpha} \quad \text{adiabatic, non-isentropic}
\]

\[
\frac{h_2}{h_1} = \left( \frac{1}{1 + \alpha} \right)^{\frac{1}{\gamma}} \quad \text{adiabatic, isentropic}
\]

\[
\alpha = \frac{m_{\text{piston}}}{P_1 A}
\]