Adiabatic Equation of State

Recall that the entropy of an ideal gas is given by

\[ S = N K_B \left[ \log \left( \frac{M}{2\pi \hbar^2} \right)^{3/2} + \log \left( \frac{T^{3/2} V}{N} \right) + \frac{5}{2} \right] \tag{1} \]

In an isentropic process we have \( V T^{3/2} = c_1 \) a constant. Using the ideal gas equation of state, keeping \( N \) constant we have \( p V^\gamma = c_2 \) with \( \gamma = 5/3 \).

**Derive this from thermodynamics:** (also done in class)

Consider an ideal gas in equilibrium of \( N \) particles in a volume \( V \) in equilibrium at a temperature \( T \): this should immediately bring to mind (i) the equation of state given by \( pV = N k_B T = \nu RT \) (where \( R \) is the universal gas constant \( R = 8.31 J/moleK \) and \( \nu \) is the number of moles) and (ii) the expression for the mean energy, \( U \), \( U = \frac{5}{2} N k_B T \) for a monatomic gas and \( U = \frac{5}{2} N k_B T \) for an ideal gas of diatomic molecules. Where does the extra \( k_B T \) per molecule come from? *Explain this clearly.*

Let a monatomic ideal gas undergo a quasistatic (reversible), adiabatic (thermally insulated so that there is no transfer of heat) process (expansion, for example). We will derive the equation which describes this process.

Start with the fundamental thermodynamic identity:

\[ dQ + dW = dU \]

where \( dQ = 0 \) since no heat transfer occurs by the statement of the problem. \( dW \) is the work done on the system and is given by \(-pdV\) (quasistatic process). Given that \( U = (5/2)N k_B T \) we obtain

\[ -pdV = \frac{5}{2} Nk_B dT \]

where we have assumed that \( N \) is fixed. This is not in a nice form; why not? It involves all three variables \( p, V, \) and \( T \). We will eliminate \( T \) and obtain an equation containing only \( p \) and \( V \). We do this by using the equation of state which yields

\[ pdV + V dp = N k_B dT \]

and thus for the adiabatic process we have

\[ -pdV = \frac{5}{2} Nk_B dT = \frac{5}{2} [pdV + V dp] \]

which can be simplified to obtain

\[ V dp = -\frac{7}{5} pdV \]
which can be integrated to yield
\[ pV^{7/5} = K \]
where \( K \) is a constant. If we had used a monatomic gas we would have obtained \( pV^{5/3} = C \) for some other constant \( C \). The exponent of \( V \) is usually denoted by \( \gamma \). If one wants to know how \( T \) and \( p \) are related in an adiabatic process simply eliminate \( p \) form \( pV^\gamma = K \) using the ideal gas equation of state.

**Useful result:** Recast the equation of state in terms of the number of moles \( \nu \) of the substance using freshman physics and chemistry. The number of moles is \( \nu = m/M \) where \( m \) is the mass of the gas in grams and \( M \) is the *molar mass* (used to be referred to as the gram molecular weight) defined as the mass per mole of the substance in grams. (The molar mass of water is approximately 18 g/mole, for example.) Recall that the gas constant is defined by \( R \equiv N_A k_B \) where \( N_A = 6.022 \times 10^{23} \) and \( R \approx 8.31 J/(mol \cdot K) \).

\[ pV = Nk_BT = \left( \frac{N}{N_A} \right) (N_Ak_B)T = \nu RT = (m/M)RT \quad (2) \]

The above implies that
\[ p = \left( \frac{m}{V} \right) \frac{RT}{M} = \frac{\rho RT}{M} \quad (3) \]
where \( \rho = m/V \) is the mass density and \( M \) is the molar mass or molecular weight.

**Temperature of the Atmosphere**

We calculate the temperature \( T \) of the atmosphere as a function of the height \( h \) above sea-level.

The main reason for variation of \( T \) with \( h \) is the existence of (large) convection currents that transport air from the lower regions to higher regions and vice versa.

(Good) Assumptions: (1) Air is an ideal gas (low density). (2) When air is transported the process can be considered to be adiabatic since air is a poor conductor of heat.

So the idea is that when air ascends from lower regions to higher regions at lower pressure it expands adiabatically, doing work in the process, extracting the energy required from its internal energy and thus its temperature decreases. As a physicist you need to check that this idea is reasonable quantitatively.

The adiabatic equation of state for an ideal gas is given by \(^1 \) \[ T^\gamma p^{(1-\gamma)} = K \] where \( K \) is a constant. Take logarithms before differentiation (useful trick to remember).

\[ \gamma \log T + (1-\gamma) \log p = C \quad (4) \]

\(^1\)Write this in terms of \( T \) and \( p \) since we have a relation between \( p \) and \( h \) from mechanical equilibrium and we can eliminate \( p \) to obtain \( T \) as a function of \( h \).
Differentiating we obtain

\[
\frac{dT}{T} = + \left( \frac{\gamma - 1}{\gamma} \right) \frac{dp}{p} \Rightarrow \frac{dT}{dp} = \left( \frac{\gamma - 1}{\gamma} \right) \frac{T}{p} = \left( \frac{\gamma - 1}{\gamma} \right) \frac{M}{\rho R} \tag{5}
\]

where we have used the equation of state in the useful form.

Now figure out how the pressure varies with height by considering the mechanical equilibrium of a slab of infinitesimal thickness of air in the presence of gravity. The equilibrium condition yields (Please derive this!) \( \frac{dp}{dh} = -\rho g \) where \( \rho \) is the density of air. Combining Eqns. 5 and the equation for \( \frac{dp}{dh} \) we obtain

\[
\frac{dT}{dh} = -\left( \frac{\gamma - 1}{\gamma} \right) \frac{gM}{R} \tag{6}
\]

We use \( \gamma = 7/5 \) since nitrogen and oxygen the predominant gases in the atmosphere are diatomic, \( g = 9.80 m/s^2 \), \( M \approx 29 g/mole \) (roughly that of nitrogen, slightly more because of Oxygen; note this is in grams), and \( R = 8.31 J/mole K \). Substituting we have

\[
\frac{dT}{dh} \approx -9.8^\circ C/km \tag{7}
\]

This value of approximately 10^\circ C per km is larger than the actual value. Incidentally, meteorologists refer to this as the *dry adiabatic lapse rate*. The chief reason for this is the neglect of water vapor condensation (releases latent heat and raises the temperature) This condensation is also the reason for cloud caps on mountains and chinook and foehn winds.

The value of the lapse rate is strongly dependent on the amount of water vapor in the air. Dry air cools at about 10 C/km (the 'dry adiabatic lapse rate'), while moist air usually cools at less than 6 C/km ('moist adiabatic lapse rate'). The word adiabatic means that no outside heat is involved in the warming or cooling of the air parcels.
In chemical thermodynamics one uses **enthalpy** since many processes occur at constant pressure. So one uses

\[ H = U + pV \]  

(8)

People usually write these equations in intensive form as specific enthalpy \( h = u + pv \) where the lower case letters refer to the quantity per mole or per kilogram or whatever.

\[ dH = TdS + Vdp + \mu dN \]  

(9)

so one has

\[ C_p = T \left( \frac{\partial S}{\partial T} \right)_p = \left( \frac{\partial H}{\partial T} \right)_p . \]

Thus a measurement of the heat capacity or specific heat per mole of the substance yields the change in enthalpy:

\[ H(T_2) - H(T_1) = \int_{T_1}^{T_2} dT C_p(T) \]  

(10)

One use differential scanning calorimetry (the temperature is continuously scanned as a function of time). There are tables of enthalpy for different substances through phase transformation including allotropes. Allotropes are different structural modifications of an element; the atoms of the element are bonded together in a different manner. Oxygen and Ozone, diamond, graphite, and graphene, etc. For compounds sometimes it is called polymorphism. How much energy does it take to convert it from one form to another.

Some numbers. At around 1 bar \((10^5 Pa \text{ close to atmospheric pressure})\) at 100\(C\) the specific volume of steam and water are 1.673\(m^3/kg\) and 0.001\(m^3/kg\) respectively. The internal energies are 2507\(kJ/kg\) and 419\(kJ/kg\) respectively. The specific enthalpy of steam is 2676\(kJ/kg\). What is \(p \Delta V = 1.01325 \times 10^5 \times 1.672 = 169.415 kJ/kg\) and 2676 − 2507 = 169\(kJ/kg\). The evaporation enthalpy is obtained as 2676 − 419 = 2257\(kJ/kg\). Note that \(\Delta H = T \Delta S\) since \(V \Delta p\) vanishes at constant pressure and so we obtain the change in entropy from this data. \(\Delta S\) is 6.048 \(kJ/(kg \cdot K)\).

Aside: recall that we used homogeneity to show that \(G \equiv U - TS + pV = N \mu\) and so we have \(dG = -SdT + Vdp = N d\mu\). At constant temperature for one mole \((v \text{ is the molar volume})\) we obtain

\[ vdp = d\mu \Rightarrow \mu - \mu_0 = \int_{p_0}^{p} dp v(p,T) . \]

(11)

For an ideal gas we obtain

\[ \mu - \mu_0 = RT \ln \left( \frac{p}{p_0} \right) \]  

(12)
for \( p \) close to \( p_0 \) we find \( \Delta \mu \propto \Delta p \) at constant temperature or more precisely the pressure is more like the fugacity \( f \equiv \exp[\mu/(RT)] \):

\[
\frac{p}{p_0} = \frac{e^{\pi \tau}}{e^{\pi \tau_0}} \equiv \frac{f}{f_0}.
\] (13)

**Diatomic molecule** Classically, the rotational energy is \( \frac{1}{2}(\omega_x^2 + \omega_y^2) \) and the vibrational potential energy is \( \frac{1}{2}\alpha z^2 \) where \( \alpha \) is the spring constant. The kinetic energies (center of mass and vibrational) are quadratic in the momenta. It is easy to note that if the energy is \( \frac{1}{2}a q^2 \), quadratic in the generalized coordinate \( q \)

\[
Z \propto \int_{-\infty}^{\infty} dq e^{-a q^2/2} \rightarrow \beta^{-1/2} \int_{-\infty}^{\infty} dq' e^{-a q'^2/2}
\] (14)

Therefore, the energy is \( -\frac{\partial}{\partial \beta} \ln Z = \frac{1}{2}k_B T \). Every quadratic degree of freedom yields an energy \( k_B T/2 \). Thus we obtain a total energy per molecule of \( (7/2)k_B T \). One writes

\[
U = \frac{1}{N} \frac{k_B T}{(\gamma - 1)} \text{ where } \gamma \equiv \frac{C_p}{C_V}
\]

See the aside below for an explanation. Thus we have \( \gamma - 1 = \frac{2}{7} \) or \( \gamma = 1.286 \). Look up results for \( \gamma \).

**Aside:** Per mole of an ideal gas we have for the enthalpy \( h = u + pv \) where the lower case letters refer to the quantities per mole. \( pv = RT \) and therefore, for an ideal gas \( h = u + RT \) and hence \( c_p = c_V + R \) where \( R = N_A k_B = 8.314 J K^{-1} mol^{-1} \). We can then write \( C_p = C_V + \nu R \) or equivalently \( C_p = C_V + N k_B \). Thus

\[
U = C_V T = \frac{C_V}{C_p - C_V} N k_B T = \frac{1}{\gamma - 1} N k_B T.
\] (15)

Experimentally \( H_2 \) and \( O_2 \) yield \( \gamma \approx 1.40 \). Iodine yields 1.30 closer to the predicted value. Note that the answer does not depend upon the rigidity of the spring or the value of the moment of inertia. Actually, \( \gamma \) depends on the temperature and varies from 1.6 to 1.30 between \(-185^\circ C \) and 2000\(^\circ C \). This was a problem and all classical fixes make the agreement worse. Nonlinear springs do not help. If we include internal degrees of freedom \( \gamma \) tends to unity. Maxwell in 1859 observed the discrepancy with the experiments! By 1890 Jeans says it is a mysterious phenomenon, it is as if certain kinds of motion “freeze out.” The answer was given by Planck and Einstein. The harmonic oscillator describing the vibrational modes has quantized energy levels and the probability of occupation of the first excited state \( e^{-\beta \hbar \omega} \) is vanishing at room temperatures and so the harmonic oscillator does not contribute. The vibrational frequencies are \( 12.5 \times 10^{13} Hz \) in \( H_2 \) or 6000\( K \), 6.43 \( \times \) \( 10^{13} Hz \) in \( CO \) and 4.7 \( \times \) \( 10^{13} Hz \) in \( O_2 \) corresponding to 2256\( K \).

The rotational energy levels are given by \( E_J = \frac{b^2 J(J+1)}{2I} \) and have separations of 2 to 3\( K \) the corresponding degrees of freedom behave classically.