3.5.6 Specific Heat

When a unit mass of gas is heated but not allowed to expand, the increase in the total heat content per unit increase of temperature is known as the specific heat at constant volume (C_v). Conversely, if the gas is allowed to expand in such a way that its pressure stays constant, additional energy is need for expansion so that the specific heat at constant pressure (C_p) is larger than (C_v).

To evaluate the difference between (C_p) and (C_v), the work done by expansion can be calculated by considering the special case of a cylinder with cross-section A fitted with a piston which applies a pressure p on the gas in the cylinder, thereby exerting a force pA. If the gas is heated and expands to push the cylinder a distance x, then the work done is the product of the force pA and the distacne x or pAx, which is also the product of the pressure p and the change of volume Ax. The same relation is valid for any system in which the gas expands at constant pressure.

The work done for a simple expansion dV of a unit mass of gas at constant pressure p is found by differentiating equation (6.22) to give

$$p\,dV = (R/M)\,dT \tag{6.24}$$

As the difference between the two specific heats is the work done in expansion per unit increase of temperature, it follows that

$$C_p - C_v = R/M \tag{6.25}$$

The ratio of C_p to C_v for gases depend on the energy associated with the vibration and rotation of its molecules and therefore depends on the number of atoms forming the molecule. For diatomic molecules such as nitrogen and oxygen which are the major constituents of air, the value of $C_p/C_v = 7/5$ and. Because $C_p - C_v = R/M$, it follows that $C_p = (7/2)\ R/M$ and $C_v = (5/2)\ R/M$. In the natural environment, most process involving heat exchange in air occur at a pressure (atmospheric) which is effectively constant and since the molecular weight of air is 28.94

$$Cp = (7/2) \times (8.31/28.94) = 1.01 J\ g^{-1}\ K^{-1}$$

6.5.7 Lapse Rate

Meteorologists apply thermodynamic principles to the atmosphere by imagining that discrete parcels of air are posted either vertically or horizontally by the action of wind or turbulence. Relations between temperature, pressure and height can be deduced by assuming that processes within a parcel are adiabatic, that is, the parcel neither gains energy from its environment nor loses energy.

Suppose a parcel containing unit mass of air makes a small ascent so that it expands as external pressure falls by dp. If there is no external supply of heat, the energy for expansion must come from cooling of the parcel by an amount dT. It is convenient to treat this as a two stage process:

(1) Parcel ascends and cools at constant pressure and volume providing energy C_v dT.

(2) Parcel expands against external pressure requiring energy p dV .

For an adiabatic process, the sum of these quantities must be zero, or

$$C_v\, dT + p\, dV = 0 \tag{6.26}$$

Differentiating equation (3.23) and putting $R/M = C_p - C_v$ gives

$$V\, dp + p\, dV = (C_p - C_v)\, dT \tag{6.27}$$

Eliminating pdV from the last two equations as follows

$$C_v\, dT + p\, dV = 0 \text{ or } p\, dV = -C_v dT$$

and $$p\, dV = (C_p - C_v)\, dT - V\, dp$$

or $$-C_v dT = C_p\, dT - C_v\, dT - V\, dp$$

or $$C_p\, dT = V\, dp \tag{6.28}$$

Since $$pV = RT/M \text{ so } V = RT/Mp$$

or $$C_p dT = \frac{RT}{Mp} dp \text{ or } \frac{dT}{T} = \left(\frac{R}{MC_p}\right)\frac{dp}{p} \tag{6.29}$$

with integration we have

$$T = p^{(R/MC_p)} \tag{6.30}$$

where $$R/MC_p = (C_p - C_v)/C_p = 0.29 \text{ for air}$$

When the change of temperature with pressure for the adiabatic ascent of a parcel has been established, the change of temperature with height can be found when the change of pressure with height is known. A layer of atmosphere with thickness dz and density ρ exerts a pressure dp equal to the weight per unit area or gρdz where g is the gravitational acceleration. Because p decreases as z increases

$$dp = -g\, \rho dz$$

and substituting for ρ from equation 6.22 gives

$$\frac{dp}{p} = -\left(\frac{gM}{RT}\right) dz \tag{6.31}$$

Substituting the value of dp/p in equation (6.28) then gives

$$\frac{dT}{dz} = -g/C_p \qquad (6.32)$$

This quantity dT/dz is known as the dry adiabatic lapse rate or DALR. When both g and C_p are expressed in SI units, the DALR is

$T = 9.8\ (\mathrm{m\ s^{-2}}) / 1.01 \times 10^3\ (\mathrm{J\ kg^{-1}\ K^{-1}}) = 0.01$ per metre or 1K per 100 metres.

Dry in this context implies that no condensation or evaporation occurs within the parcel. A wet adiabatic lapse rate operates within clouds where the lapse rate is smaller than the DALR, because of the release of latent heat by condensation.

The difference between the actual lapse rate of air and the DALR is a measure of the vertical stability of the atmosphere. During the day, the lapse rate up to a height of 1km is usually larger than the DALR and is many times larger immediately over dry sunlit surfaces. Consequently ascending parcels rapidly become warmer than their surroundings and experience buoyancy which accelerates their ascent and promotes turbulent mixing so that the atmosphere is said to be unstable. Conversely, temperature usually increases with height at night ('inversion' of the day time lapse rate) so that rising parcels become cooler than their environment and further ascent is inhibited by buoyancy. Turbulence is suppressed and the atmosphere is said to be stable.

The significance lies in the fact that during the day when the atmospheric conditions are unstable, the atmosphere will promote active mixing of its contents or the materials (pollutants) released in it.

At night when there is a temperature inversion and the buoyancy of the surrounding environment inhibits the ascent of rising parcels of air, stable conditions develop, so any pollutant released into the atmosphere does not move to great heights or undergo active mixing. The load of pollutants thus sinks down towards the earth's surface in the form of a pollution blanket consisting of waste gases, fumes and particulate matter.