Lecture 9 Internal Energy, Specific Heat Capacities, and Enthalpy

(Ref.: Sec.3.4, Hess)

9.1 Internal Energy

Q: What is the change in internal energy "du" in the First Law of Thermodynamics (3.20)?

$$dq = du + pd\alpha. \tag{3.20}$$

For a real gas, the internal energy is a function of all three basic state variables:

$$u = u(p, \alpha, T) \tag{3.21}$$

For an ideal gas, p, α, and T are not independent (related via the equation of state), so u is only a function of two state variables, such as α, T:

$$u = u(\alpha, T) \tag{3.22}$$

Thus, the change of u (Δu or the exact differential of u, i.e. du) may be written

$$du = \frac{\partial u}{\partial \alpha} d\alpha + \frac{\partial u}{\partial T} dT , \tag{3.23}$$

where du: the change in specific internal energy;
$\partial u / \partial \alpha$:   the rate of change of u with α when T is held constant;

$\partial u / \partial T$: the rate of change of u with T when α is held constant.

Substituting (3.23) into the first law of thermodynamics (3.20)

$$dq = du + pd\alpha. \tag{3.20}$$

gives

$$\frac{\partial u}{\partial \alpha} d\alpha + \frac{\partial u}{\partial T} dT = dq - pd\alpha. \tag{3.24}$$

The above equation may be rewritten as

$$dq = \frac{\partial u}{\partial T} dT + \left(\frac{\partial u}{\partial \alpha} + p \right) d\alpha. \tag{3.25}$$

For an isosteric process (α is constant), the above equation reduces to
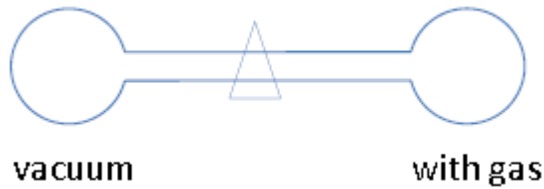
$$dq = \frac{\partial u}{\partial T} dT,$$

or

$$\frac{\partial u}{\partial T} = \left(\frac{dq}{dT} \right)_\alpha \equiv c_v. \tag{3.26}$$

Thus, Eq. (3. 23) can be rewritten as

$$du = \frac{\partial u}{\partial \alpha} d\alpha + c_v dT \tag{3.27}$$

Note that $\partial u / \partial \alpha$ can be measured experimentally as follows.

vacuum   with gas

When the valve is opened suddenly, the gas will expand into the evacuated vessel and is against zero pressure. Therefore, there is no work done and no heat is taken away. That is, $dw=0$ and $dq=0$. Based on the first law, $du=0$. Thus, Eq. (3.27) becomes

$$\frac{\partial u}{\partial \alpha} = -c_v \frac{\partial T}{\partial \alpha}. \qquad (3.28)$$

In the above, we have applied

$$\frac{dT}{d\alpha} = \frac{\partial T}{\partial \alpha}.$$

This is due to constant pressure in the above experiment,

$$dT = \frac{\partial T}{\partial p} dp + \frac{\partial T}{\partial \alpha} d\alpha = \frac{\partial T}{\partial \alpha} d\alpha.$$

Experiments performed by Joule and Thomson showed that

[Joule-Thomson Effects] A small heat exchange (cooling) occurs in the experiments due to the work done by some portions of the gas against others.

However, this effect is very small and vanished for ideal gas, i.e.

$$\frac{\partial u}{\partial \alpha} = 0.$$

Thus

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$$\frac{\partial u}{\partial \alpha} = -c_v \frac{dT}{d\alpha} = 0. \tag{3.29}$$

Substituting Eq. (3.29) into the first law of thermodynamics, i.e. Eq. (3.27), leads to

$$du = c_v dT, \tag{3.30}$$

for ideal gas. That is, the internal energy of an ideal gas is a function of temperature only, provided c_v is at most of function of temperature only.

In fact, c_v is a function of temperature only. Note that for an ideal gas

$$c_v = c_v(\alpha, p, T) = c_v(\alpha, T).$$

so

$$\frac{\partial c_v}{\partial \alpha} = \frac{\partial}{\partial \alpha}\left(\frac{\partial u}{\partial T}\right) = \frac{\partial}{\partial T}\left(\frac{\partial u}{\partial \alpha}\right) = 0,$$

where Eqs. (3.26) and (3.29) have been used. Therefore, c_v is not a function of α. That is to say,

$$c_v = c_v(T).$$

Finally, first law of thermodynamics of an ideal gas may be written

$$dq = c_v dT + p d\alpha. \tag{3.31}$$

9.2 Specific Heat Capacities of an Ideal Gas

We have derived the first law of thermodynamics of ideal gases:

$$dq = c_v dT + pd\alpha. \tag{3.31}$$

For ideal gases, we may apply the equation of state,

$$p\alpha = RT \tag{3.32}$$

Taking differentiation on (3.32) yields

$$pd\alpha + \alpha dp = RdT$$

or

$$pd\alpha = RdT - \alpha dp. \tag{3.33}$$

Substituting (3.33) into (3.31) we get,

$$dq = (c_v + R)dT - \alpha dp. \tag{3.34}$$

Consider an isobaric process ($dp = 0$), (3.34) gives

$$c_v + R = \left.\frac{dq}{dT}\right|_p,$$

which is nothing but c_p, i.e.,

$$c_p = c_v + R. \tag{3.35}$$

For dry air, we have

$$c_p = 1004 J\ K^{-1} kg^{-1}$$

$$c_v = 717 \, J \, K^{-1} kg^{-1}$$

$$R = 287 \, J \, K^{-1} kg^{-1}.$$

In general, we have

$$c_p : c_v : R = 5 : 3 : 2 \qquad \text{for an ideal monatomic gas,}$$

$$c_p : c_v : R = 7 : 5 : 2 \qquad \text{for an ideal diatomic gas.}$$

Dry air is nearly an ideal diatomic gas since N_2 and O_2 contribute more than 97% of its composition.

Thus, the first law of thermodynamics may also be written as

$$dq = c_p dT - \alpha dp. \tag{3.36}$$

Equation (3.36) is especially useful because dT and dp are easily obtained from daily meteorological observations.

Note that $c_p dT$ **is not** the change in internal energy ($c_v dT$), and αdp **is not** the amount of work done ($pd\alpha$).

9.3 Enthalpy

Equation (3.31)

$$dq = c_v dT + pd\alpha. \tag{3.31}$$

can be rewritten as

$$dq = c_v dT + d(p\alpha) - \alpha dp.$$

This implies

$$dq = du + d(p\alpha) - \alpha dp \text{ or } dq = d(u + p\alpha) - \alpha dp. \qquad (3.37)$$

Thus, the 1st law of thermodynamics can be written as above.

➤ For isobaric processes (air parcel moving along isobaric surfaces), $dp=0$, so

$$dq = d(u + p\alpha). \qquad (3.38)$$

For convenience, we may define a new variable h such that

$$h = u + p\alpha. \qquad (3.39)$$

which is called <u>enthalpy</u>.

Using the concept of enthalpy, the 1st law can now be written as

$$dq = dh - \alpha dp. \qquad (3.40)$$

For isobaric processes, it implies

$$dq = dh.$$

Thus, comparing (3.36) with (3.40) gives

$$dh = c_p dT. \qquad (3.41)$$

Note that $c_v dT$ is the change in internal energy, while $c_p dT$ is the change in enthalpy (dh). In other word, *$c_p dT$ is the heat exchange in an isobaric process.*

Many meteorological processes are nearly isobaric (so we need to use c_p), thus enthalpy is more convenient than internal energy ($c_v dT$).