

ESO201A
Lecture#16
(Class Lecture)

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(8)

Specific Heat Relations of Ideal Gases

For a quasi-equilibrium reversible process, the first law is

$$\delta q - p dv = du$$

$$\text{or } \delta q = du + p dv$$

and
$$c_v = \left(\frac{du}{dT} \right)_v$$

In the special case of the ideal gas, $u = f(T)$ only; therefore,

$$c_v = \frac{du}{dT}$$

and
$$\boxed{\delta q = c_v dT + p dv} \quad (1)$$

Now, all equilibrium states are represented by the ideal-gas equation,

$$p v = R T$$

and for a quasi-equilibrium reversible process

$$p dv + v dp = R dT \quad (2)$$

(9)

Substituting eq. (2) in eq. (1),
we get

$$\delta q = (C_v + R) dT - v dp$$

and dividing by dT yields

$$\frac{\delta q}{dT} = C_v + R - v \frac{dp}{dT}$$

At constant pressure, the left hand side becomes C_p and $dp = 0$; therefore,

$$\boxed{C_p = C_v + R}$$

(3)

$$\text{or } C_p - C_v = R$$

The reason that C_p is always greater than C_v is the following:

As heat is supplied to the system at constant pressure, the gas expands and works against the external pressure, which of course, is equal to the pressure of the gas in a quasi-equilibrium reversible process.

Thus, c_p includes work of expansion, which is not found in the constant volume ($\int P dv = 0$) specific heat, c_v .

Since $u = f(T)$ only for an ideal gas, it follows that

$$c_v = \frac{du}{dT} = f(T) \text{ alone,}$$

and so $c_p = c_v + R = f(T) \text{ alone.}$

Experimental Determination of Specific Heats

The specific heats of real gases are measured by the electrical method. To measure c_v , the gas is contained in a thin-walled steel flask with a heating wire wound around it. By maintaining an electric current in the wire, an equivalent amount of heat is supplied to the gas, and the specific heat at constant volume is obtained by measuring the temperature rise of the gas: $Q = m c_v (T_2 - T_1)$. The same method is used to measure c_p except that, instead of confining the gas to a constant volume, the gas is allowed to flow at constant pressure through a calorimeter, where it receives heat electrically per unit time. From the inlet and outlet temperatures, the rate of heat

transfer, and the mass flow rate of the gas, the value of c_p is obtained.

The relevant equation is: $\dot{Q} = \dot{m} c_p (T_{outlet} - T_{inlet})$

$$\text{or } c_p = \frac{\dot{Q}}{\dot{m} (T_{outlet} - T_{inlet})}$$

The results of such measurements at low pressures, that is, ideal gases, can be stated in a simple manner in terms of molar specific heats.

1. All Ideal Gases

- (a) $\bar{c}_v = f(T)$ only.
- (b) $\bar{c}_p = f(T)$ only, and is greater than \bar{c}_v .
- (c) $\bar{c}_p - \bar{c}_v$ is not a function of T , but equal to R_u .

That is, $\bar{c}_p - \bar{c}_v = R_u$.

where $R_u = 8.315 \text{ J/moleK}$ or 8.315 kJ/kmoleK .

- (d) $\frac{\bar{c}_p}{\bar{c}_v} = \gamma$ is a function of T only, and is greater than 1.

2. Monatomic Gases, such as He, Ne, and Ar, and most metallic vapours, such as the vapours of Na, Cd, and Hg:

(a) \bar{C}_v is constant over a wide temperature range and is very nearly equal to $\frac{3}{2} R_u$.

(b) \bar{C}_p is constant over a wide temperature range and is very nearly equal to $\frac{5}{2} R_u$.

(c) The ratio $\frac{\bar{C}_p}{\bar{C}_v} = \kappa$ is constant over a wide temperature range and is very nearly equal to $\frac{5}{3} = 1.667$.

3. So-called Permanent Diatomic gases, namely, air, H_2 , D_2 , O_2 , N_2 , NO , and CO :

(a) \bar{C}_v is constant at ordinary temperatures, being equal to about $\frac{5}{2} R_u$, and increases as the temperature is raised.

(b) \bar{C}_p is constant at ordinary temperatures, being equal to about $\frac{7}{2} R_u$, and increases as the temperature is raised.

(c) the ratio, $\frac{\bar{C}_p}{\bar{C}_v} = \gamma$ is constant at ordinary temperatures, being equal to about $\frac{7}{5}$ ($= 1.4$) and decreases as the temperature is raised.

4. Polyatomic gases (CO_2 , NH_3 , CH_4) and gases that are chemically active (Cl_2 , Br_2).

(a) \bar{C}_p , \bar{C}_v , and \bar{C}_p/\bar{C}_v vary with the temperature, the variations being different for each gas.

Internal Energy, Enthalpy, and Specific Heats of Solids and Liquids

Incompressible Substance

A substance whose specific volume (or density) is constant is called an incompressible substance. The specific volumes of solids and liquids essentially remain constant during a process. Therefore, liquids and solids can be approximated as incompressible substances without sacrificing much accuracy. The constant-volume assumption should be taken to imply that the energy associated with the volume change is negligible compared with other forms of energy.

Internal Energy

If a substance is incompressible, its pressure can be increased a finite amount by an infinitesimal decrease in volume, which would

not result in a significant amount of energy transfer as work.

The only means for reversibly changing the internal energy of such an idealized solid or liquid is by transfer of energy as heat.

While the pressure is involved in energy transfers to the bulk fluid (flow work), which show up in increased bulk kinetic and potential energy, it is not involved in energy transfer to the "hidden microscopic modes", and consequently, does not alter the internal energy. Thus, $u = u(T)$ only, for solids and liquids, just like ideal gases.

Specific Heat

Since $\int p dv = 0$ for solids and liquids, $c_p = c_v = c$.

Hence, $du = c dT = c(T) dT$
 $\Delta u = u_2 - u_1 = \int_1^2 c(T) dT$

The variation of specific heat, c , with temperature should be known before this integration can be carried out. For small temperature intervals, a 'c' value at the average temperature $\left(\frac{T_1 + T_2}{2}\right)$ can be used and treated as a constant, yielding

$$\Delta u = c_{avg} (T_2 - T_1)$$

Enthalpy changes

Using the definition of $h = u + Pv$ and noting that $v = \text{constant}$, the differential form of the enthalpy change of incompressible substances can be determined by differentiation to be

$$\begin{aligned} dh &= du + v dp + \cancel{p dv} \\ &= du + v dp \end{aligned}$$

Integrating,

$$\begin{aligned} \Delta h &= \Delta u + v \Delta p \\ &= c_{avg} \Delta T + v \Delta p \\ \Rightarrow h_2 - h_1 &= c_{avg} (T_2 - T_1) + v (p_2 - p_1) \end{aligned}$$

Hence, we can conclude that the enthalpy of an incompressible substance, unlike the enthalpy of an ideal gas, is a function of both temperature and pressure, that is, $h = f(T, P)$.

Solids

For solids, the term $v\Delta P$ is insignificant since v is very small and thus $\Delta h = \Delta u = c_{avg} \Delta T$.

Liquids

For liquids, two special cases are commonly encountered:

1. Constant-pressure processes, as in heaters ($\Delta P = 0$):

$$\Delta h = \Delta u = c_{avg} \Delta T$$

2. constant-temperature processes, as in pumps ($\Delta T = 0$): $\Delta h = v\Delta P$.

For a process between states 1 and 2, we can then write

$$\boxed{h_2 - h_1 = v(P_2 - P_1)}$$