

## Lecture 4

### Enthalpy

In many thermodynamic analyses the sum of the internal energy  $U$  and the product of pressure  $p$  and volume  $V$  appears. Because the sum  $(U + pV)$  occurs so frequently, it is convenient to give the combination a name. The combination  $(U + pV)$  is therefore defined as **enthalpy**  $H$ .

$$\text{Or } h = u + pv \text{ (J/kg)}$$

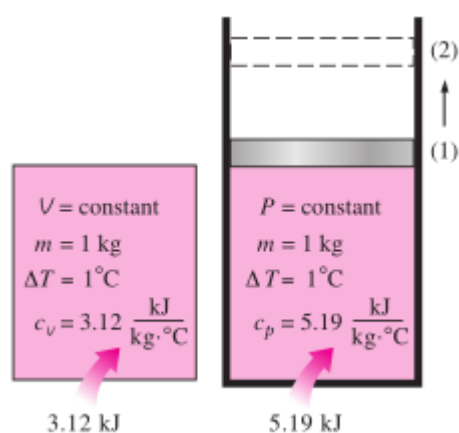
The widespread use of the property enthalpy is due to Professor Richard Mollier, who recognized the importance of the group  $u + Pv$  in the analysis of steam turbines (first law analysis of open systems). Mollier referred to the group  $u + Pv$  as heat content and total heat. But we know that heat is energy in transit and the word heat content or total heat of a system does not have any meaning in modern thermodynamic terminology. So these terms were replaced in 1930s by the term enthalpy.

### Specific Heats

It takes different amounts of energy to raise the temperature of identical masses of different substances by one degree. Therefore, it is desirable to have a **property** that will enable us **to compare the energy storage capabilities of various substances**. This property is the **specific heat**.

The specific heat is defined as the energy required to raise the temperature of a unit mass of a substance by one degree.

There are two kinds of specific heats: **specific heat at constant volume**  $c_v$  and **specific heat at constant pressure**  $c_p$



The specific heat at constant volume  $c_v$  is the energy required to raise the temperature of the unit mass of a substance by one degree as the volume is maintained constant. The energy required to do the same as the pressure is maintained constant is the specific heat at constant pressure  $c_p$

The specific heat at constant pressure  $c_p$  is **always greater than  $c_v$**  because at constant pressure the system is allowed to expand and the **energy for this expansion work must also be supplied** to the system.

Equations for  $c_v$  and  $c_p$

By the definition of  $c_v$

$$c_v = \frac{1}{m} \left( \frac{\partial Q}{\partial T} \right)_v$$

First law states that  $\delta Q - \delta W = dU$  or  $\delta Q = \delta W + dU$ . For a constant volume process  $\delta W = 0$

$\delta Q = dU$  for a constant volume process. Therefore  $c_v = \frac{1}{m} \left( \frac{\partial U}{\partial T} \right)_v$  or

$c_v = \left( \frac{\partial u}{\partial T} \right)_v \quad \frac{\text{J}}{\text{kgK}}$
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For a constant pressure process with expansion work  $\delta W = p dV$

$\delta Q = p dV + dU$ . Integrating the above expression we get  
 $Q = p(V_2 - V_1) + (U_2 - U_1) = (U_2 + p_2 V_2) - (U_1 + p_1 V_1)$

$$(U + pV) = H$$

Therefore  $Q = H_2 - H_1$  or  $\delta Q = dH$

Now

$$c_p = \frac{1}{m} \left( \frac{\partial Q}{\partial T} \right)_p \text{ but for a constant pressure process } \delta Q = dH$$

$$\text{Therefore } c_p = \frac{1}{m} \left( \frac{\partial H}{\partial T} \right)_p \text{ or}$$

$c_p = \left( \frac{\partial h}{\partial T} \right)_p \quad \frac{J}{kgK}$
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$c_p$  and  $c_v$  are expressed in terms of other properties in the above equations. Therefore they must be properties. Since the above equations are property relations they are independent of the type of process.

### Internal energy and Enthalpy of ideal gases

Ideal gas is a gas whose temperature, pressure and specific volume are related by  $pV = RT$ . For an ideal gas the internal energy is a function of the temperature only. Using the definition of enthalpy and the equation of state of an ideal gas, we have  $h = u + pv$ .

$Pv = RT$ . Therefore  $h = u + RT$ . Since  $u$  is a function of temperature only it follows that enthalpy is also a function of temperature only for an ideal gas.

The equations  $c_v = \left( \frac{\partial u}{\partial T} \right)_v$  and  $c_p = \left( \frac{\partial h}{\partial T} \right)_p$  can now be written as

$$c_v = \frac{du}{dT} \text{ and } c_p = \frac{dh}{dT}$$

Since  $u$  and  $h$  are only functions of temperature only and not functions of volume or pressure there is no need to keep the volume or pressure constant as it is not going to affect the change in internal energy or enthalpy. So partial derivatives can be replaced by ordinary derivatives.

From the above equations we get

$$du = c_v dT \quad \text{and} \quad dh = c_p dT \text{ for ideal gases}$$

### Relationship between $c_p$ and $c_v$ for ideal gases

For ideal gases  $h = u + RT$

$$dh = du + R dT$$

$$c_p dT = c_v dT + R dT$$

Dividing by dT we get

$$c_p - c_v = R$$

The specific heat ratio  $\gamma$ , defined as  $\gamma = \frac{c_p}{c_v}$

For monatomic gases, its value is essentially constant at 1.667. Many diatomic gases, including air, have a specific heat ratio of about 1.4 at room temperature.

How to compute approximate values of  $c_p$  and  $c_v$  when no data is available

For monatomic gases (eg. He, Ne, Ar etc.)

$$c_v = \frac{3}{2}R \quad c_p = c_v + R = \frac{5}{2}R \quad \gamma = \frac{c_p}{c_v} = 1.667$$

For diatomic gases (eg. O<sub>2</sub>, N<sub>2</sub>, air etc.)

$$c_v = \frac{5}{2}R \quad c_p = c_v + R = \frac{7}{2}R \quad \gamma = \frac{c_p}{c_v} = 1.4$$

For polyatomic gases (eg. CO<sub>2</sub>)

$$c_v = 3R \quad c_p = c_v + R = 4R \quad \gamma = \frac{c_p}{c_v} = 1.3$$

### Specific heats of solids and liquids

Solid and liquids are **incompressible substances**, which mean that their specific volume does not change during a process. The constant-volume and constant-pressure specific heats are identical for incompressible substances.

Therefore, for solids and liquids, the subscripts on  $c_p$  and  $c_v$  can be dropped, and both specific heats can be represented by a single symbol  $c$

$c_p = c_v = c$  for incompressible substances.

### Adiabatic process for an ideal gas

An adiabatic process is a process where heat transfer is zero.  $Q = 0$  for adiabatic process. Therefore first law can be written as  $0 = du + pdv$

$$c_v dT = -pdv$$

$$\gamma c_v dT = -\gamma pdv \quad (\text{multiplying } \gamma \text{ on both sides})$$

$$c_p dT = -\gamma pdv \dots\dots\dots(1) \quad (\text{since } \gamma = \frac{c_p}{c_v})$$

$$h = u + pv$$

$$dh = \underline{du} + \underline{pdv} + vdp \quad (\text{the underlined terms are zero for an adiabatic process.})$$

$$c_p dT = vdp \dots\dots\dots(2) \quad (\text{for an ideal gas } dh = c_p dT)$$

from equations (1) and (2)

$$-\gamma p dv = v dp$$

$$-\gamma \frac{dv}{v} = \frac{dp}{p}$$

Integrating the above equation for the adiabatic process from state 1 to 2 we get

$$-\gamma \ln \frac{v_2}{v_1} = \ln \frac{p_2}{p_1} \quad \text{or} \quad \ln \left( \frac{v_1}{v_2} \right)^\gamma = \ln \frac{p_2}{p_1}$$

Taking exponentials and cross multiplying we get  $p_1 v_1^\gamma = p_2 v_2^\gamma$

Or  $p v^\gamma = \text{constant}$  for an adiabatic process