

Fundamentals of Thermodynamics

Lecture 7: Enthalpy and Specific Heat

ENTHALPY

- U and V are not the only state variables that we can use to characterize a thermodynamic system. We can choose other variables that can be related to U and V , such as T , p , or S .
- One commonly used state variable is called *enthalpy*, and is defined as

$$H = U + pV$$

Definition: Enthalpy is the measurement of energy in a thermodynamic system. The quantity of enthalpy equals to the total content of heat of a system, equivalent to the system's internal energy plus the product of volume and pressure.

- The differential of H is given as $dH = dU + pdV + Vdp$. This makes it possible to write the first law of thermodynamics as

$$dH = dQ + Vdp \quad (1)$$

Why Bother with Enthalpy?

- The reason enthalpy is convenient to use is that for constant pressure processes, $dp = 0$ and so $dH = dQ$.
 - Most of the thermodynamic processes in the atmosphere occur at constant pressure.
- From the first law of thermodynamics, $dU = dQ - pdV$, we see that at constant volume, $dU = dQ$.

Q. Is enthalpy the same as heat? No !

Heat (Q) is **energy in transfer** due to temperature difference. Enthalpy (H) is a **state property** of a substance.

- Heat is not stored.
- Enthalpy is stored in a substance (like internal energy)

Q. Is enthalpy the same as internal energy? No !

Internal energy is the **energy stored inside the molecules** of a substance: Kinetic (molecular motion, potential (intermolecular forces). It depends on the state (T , P , etc.) and does not include any work the system must do to push the surroundings.

Enthalpy is the internal energy plus the energy required for the system to:

- Push the surrounding atmosphere out of the way (this is called flow work or PV work).

Why they are different?

When a fluid flows (e.g. in turbines, compressors, pumps), it must **push itself into and out of** the device.

Internal energy alone cannot describe this. Enthalpy includes this "pushing energy." So it is perfect for flow systems.

Heat Capacities and Specific Heats in Terms of Enthalpy

- Heat capacity at constant volume process or a constant pressure process,

$$C_v = \left(\frac{dQ}{dT} \right)_v \quad (2)$$

$$C_p = \left(\frac{dQ}{dT} \right)_p \quad (3)$$

- From the two forms of the first law we can show that

$$\left(\frac{dQ}{dT} \right)_v = \left(\frac{dU}{dT} \right)_v$$

$$\left(\frac{dQ}{dT} \right)_p = \left(\frac{dU}{dT} \right)_p$$

so that the definitions for heat capacity can also be written as

$$C_v = \left(\frac{dU}{dT} \right)_v \quad (4)$$

$$C_p = \left(\frac{dH}{dT} \right)_p \quad (5)$$

- Heat capacity is an extensive property. Its intensive counterpart is called *specific heat*, and is defined as

$$c_v = \frac{C_v}{m} = \left(\frac{\partial u}{\partial T} \right)_v \quad (6)$$

$$c_p = \frac{C_p}{m} = \left(\frac{\partial h}{\partial T} \right)_p \quad (7)$$

- Heat capacities and specific heats are not constant, but are functions of T and p.

Relation between C_v and C_p

To see the relation between C_v and C_p , we start with the relation:

$$C_p - C_v = \left(\frac{dH}{dT}\right)_p - \left(\frac{dU}{dT}\right)_v \quad (8)$$

From the definition of enthalpy,

$$H = U + pV$$

we take the partial derivative with respect to T at constant pressure to get

$$\left(\frac{\partial H}{\partial T}\right)_p = \left(\frac{\partial U}{\partial T}\right)_p + p\left(\frac{\partial V}{\partial T}\right)_p \quad (9)$$

Substituting (9) into (8) we get

$$C_p - C_v = \left(\frac{\partial U}{\partial T}\right)_p + p\left(\frac{\partial V}{\partial T}\right)_p - \left(\frac{\partial U}{\partial T}\right)_v \quad (10)$$

The differential of U is

$$dU = \left(\frac{\partial U}{\partial T}\right)_v dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

Dividing by dT gives

$$\frac{dU}{dT} = \left(\frac{\partial U}{\partial T}\right)_v + \left(\frac{\partial U}{\partial V}\right)_T \frac{dV}{dT}$$

and assuming constant pressure we get

$$\left(\frac{dU}{dT}\right)_p = \left(\frac{\partial U}{\partial T}\right)_v + \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{dV}{dT}\right)_p$$

or

$$\left(\frac{\partial U}{\partial T}\right)_p = \left(\frac{\partial U}{\partial T}\right)_v + \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p \quad (11)$$

Substituting this into (10) gives

$$C_p - C_v = \left[\left(\frac{\partial U}{\partial T}\right)_T + p \right] \left(\frac{\partial V}{\partial T}\right)_p \quad (12)$$

In terms of specific heats this is

$$c_p - c_v = \left[\left(\frac{\partial u}{\partial T}\right)_T + p \right] \left(\frac{\partial \alpha}{\partial T}\right)_p \quad (13)$$

$$\left(\frac{\partial U}{\partial V}\right)_T \quad \left[\text{or} \left(\frac{\partial u}{\partial \alpha}\right)_T\right]$$

is called the **internal pressure**, due to forces between the molecules of the substance.

- For gases, C_p is greater than C_v . This is because in a constant-pressure process some of the heat added will be used to do work as the system expands, so the internal energy cannot increase as much as in a constant-volume process.

Specific Heats for Ideal Gases

Recall that the specific heat at constant volume was defined as

$$C_v = \left(\frac{\partial u}{\partial T} \right)_v$$

and the specific heat at constant pressure was defined as

$$C_p = \left(\frac{\partial h}{\partial T} \right)_p$$

o Since the internal energy and enthalpy of an ideal gas depend only on temperature, then for an ideal gas we don't have to write the specific heats as partial derivatives, but can instead use full derivatives

$$c_v = \frac{\partial u}{\partial T}$$

$$c_p = \frac{\partial h}{\partial T}$$

o From the expressions of the internal energy of ideal gases, we then get that

$c_v = \frac{3}{2} \dot{R}, \quad \text{monatomic gas}$
$c_v = \frac{5}{2} \dot{R}, \quad \text{diatomic gas}$

The expression relating the specific heats at constant pressure and at constant volume is also greatly simplified for an ideal gas. The general expression [Eqn. (13)] becomes, for an ideal gas,

$$c_p - c_v = \dot{R} \quad (14)$$

which tells us that

$c_p = \frac{5}{2} \dot{R}, \quad \text{monatomic gas}$
$c_p = \frac{7}{2} \dot{R}, \quad \text{diatomic gas}$

- 99 % of the atmosphere is composed of diatomic molecules (N₂ and O₂), and has a specific gas constant of 287.1 J kg⁻¹ K⁻¹. This leads to values of c_v and c_p of 718 J kg⁻¹ K⁻¹ and 1005 J kg⁻¹ K⁻¹. These values are extremely close to the measured values for the atmosphere.

The First Law of Thermodynamics for Ideal Gases

- The specific heats for ideal gasses are

$$c_v = \frac{\partial u}{\partial T}$$

$$c_p = \frac{\partial h}{\partial T}$$

From these we can write

$$du = c_v dT$$

$$dh = c_p dT$$

Using these expressions in the first law of thermodynamics results in the following two forms for the first law

$$\begin{aligned} c_v dT &= dq - p d\alpha \\ c_p dT &= dq + \alpha dp \end{aligned}$$

First law of thermodynamics for ideal gas

- We are often most interested in how the thermodynamic variables change with time. By dividing the first law by dt we get

$$\begin{aligned} c_v \frac{dT}{dt} &= \frac{dq}{dt} - p \frac{d\alpha}{dt} \\ c_p \frac{dT}{dt} &= \frac{dq}{dt} + \alpha \frac{dp}{dt} \end{aligned}$$

First law of thermodynamics for ideal gas

Exercises

1. Show that for an ideal gas

$$c_p - c_v = \left[\left(\frac{\partial u}{\partial \alpha} \right)_T + p \right] \left(\frac{\partial \alpha}{\partial T} \right)_p$$

reduces to

$$c_p - c_v = \dot{R}$$

2. Show that for an ideal gas

$$C_p - C_v = nR$$