

# Intermediate Thermodynamics

## Definitions and the First Law

### Definitions:

We will refresh some basic definitions that are used through the course.

**System** is a region in space bounded by an arbitrary surface defining a **boundary**.

The **environment or surroundings** is the physical space outside the system.

A **closed system** cannot exchange mass with the surroundings. For analysis purposes, a **control volume** (CV) containing the system may be defined and in that case a **control surface** is used to define the boundary of the control volume.

The **properties** describe the condition of a system. The properties can be classified in a) directly measurable (pressure, temperature), b) defined by laws of thermodynamics (entropy) and c) defined as combination of other properties (Gibbs function). With a subset of independent properties we can describe the condition or **state** of a system. All other properties can be calculated from this subset. The properties can be defined when a system is in equilibrium.

A transformation of a system from one equilibrium state to another is a **process**. Several different processes can lead to the same end states. The initial and final conditions of a system are the **end states**. The series of states between end states define the **path** of the process. Processes that are infinitesimally close to equilibrium at all times are called **quasistatic**.

A **simple system** is one in which there is only one way to alter the energy by work. Examples are simple compressible systems, simple elastic systems or simple electric systems.

The change in the properties when a system undergoes a process between two end states is independent of the path. Thus, the value of a property is independent of the process and depends only on the state of the system. Quantities that depend on the nature of the process are not properties. Some important quantities that are not properties are heat, work, entropy production.

An **extensive** property is one that is dependent on the size of a system, such as energy and volume. An **intensive** property can be defined locally and therefore is independent of the size of the system. Examples are temperature and pressure. Extensive properties are converted into intensive properties by dividing by the mass, leading to **specific** properties (per unit mass).

**Intrinsic** properties depend on the nature of the substance composing the system, such as temperature and pressure. Those properties independent of the nature of the substance of the system are **extrinsic**, such as velocity, electric field, etc.

The **phase** of a system describes a quantity of matter that is homogeneous in chemical composition and physical structure. Phases are separated by phase boundaries. **Single-phase** systems are formed by a single physical structure (solid, liquid or gas) and a single chemical composition. Examples are ice, liquid water or vapor, a water/alcohol mixture, etc. **Multiphase** systems involve two or more phases either in physical structure or chemical composition. Some examples are water/vapor and water/oil mixtures.

### **Energy conservation:**

The energy conservation for a closed system can be stated as:

$$Q + W = \Delta E \quad (1)$$

with  $Q$  and  $W$  the heat and work interactions (positive if acting into the system) and  $E$  is the energy inside the system. The energy usually comprises internal energy, potential energy and kinetic energy:

$$E = U + m g z + \frac{1}{2} m V^2 \quad (2)$$

The energy balance on a control volume results in:

$$\frac{dE}{dt} = \dot{Q} + \dot{W} + \sum_{in} m_{in} \left( h + \frac{V^2}{2} + g z \right)_{in} - \sum_{out} m_{out} \left( h + \frac{V^2}{2} + g z \right)_{out} \quad (3)$$

with  $h = u + p v$  the specific enthalpy.

### **Entropy:**

The fundamental relation between entropy and the heat exchange on a boundary at constant temperature  $T$  is:

$$dS = \frac{\delta Q}{T} + \sigma \quad (4)$$

where  $\sigma \geq 0$  is the entropy generation due to internally irreversible processes. Thus, in an internally reversible process we have:

$$\Delta S = \int_1^2 \left( \frac{\delta Q}{T} \right)_{\text{int rev}} \quad (5)$$

For a heat reservoir, which is defined as a reversible and constant temperature closed system, we have  $\Delta S = Q/T$ . Eq. (5) implies that in an isolated or adiabatic system we will have:

$$dS \geq 0 \quad (6)$$

### **Uncoupled and coupled systems:**

In an *uncoupled* system the different types of work interactions are independent, and also independent of the heat interactions. In the of a closed system case we can write:

$$Q + W_1 + W_2 + \dots = \Delta U + \Delta E_1 + \Delta E_2 + \dots \quad (7)$$

A simple example is an incompressible mass that changes from state  $(z_1, V_1, T_1)$  to state  $(z_2, V_2, T_2)$  without any dissipative interaction,

$$\begin{aligned} Q &= \Delta U = m c (T_2 - T_1) \\ W_1 &= \Delta E_1 = m (V_2^2 - V_1^2) / 2 \\ W_2 &= \Delta E_2 = m g (z_2 - z_1) \end{aligned} \quad (8)$$

In a *conservative* uncoupled system the work processes are irreversible, resulting in the condition:

$$\oint \delta W = 0; \quad \oint \delta Q = 0 \quad (9)$$

Real systems are non-conservative, since necessary dissipative effects are present.

A *coupled* system is one in which one or more of the energy storage modes are affected by more than one work and heat interactions. Especially important is the case in which the internal energy can be affected by work and heat interactions. All energy conversion systems work as coupled systems. For these applications (heat engines), we want a fluid with mechanical and thermal properties as strongly coupled as possible. This is the reason why gases are used as working fluids in gas turbines, spark ignition and compression ignition engines.

In terms of intrinsic and extrinsic energies, we can write:

$$\delta Q + \delta W^{ext} + \delta W^{int} = dE^{ext} + dE^{int} \quad (10)$$

Note that heat transfer affects only the intrinsic state of a substance. The kinetic energy can be calculated as the sum of the translational and rotational energy of the system respect to the center of mass plus the internal kinetic energy of the particles comprising the system:

$$E_{tot}^{KE} = E_{trans}^{ext} + E_{rot}^{ext} + U_{KE}^{int} \quad (11)$$

which has been divided into extrinsic and intrinsic contributions accordingly with the definitions stated before. The potential energy can be written as:

$$E_{tot}^{PE} = E_{grav}^{ext} + E_{elec}^{ext} + E_{mag}^{ext} + U_{PE}^{int} \quad (12)$$

where the extrinsic terms include gravitational, static and dynamic charge forces, and the intrinsic term includes the potential energy of the particles within the system. Using Eqs. (10), (11) and (12) we can write:

$$\delta Q + \delta W^{ext} + \delta W^{int} = dU^{int} + dE_{tran}^{ext} + dE_{rot}^{ext} + dE_{grav}^{ext} + dE_{elec}^{ext} + dE_{mag}^{ext} \quad (13)$$

where the internal energy covers all the intrinsic terms. Dropping the extrinsic (uncoupled terms) we get:

$$\delta Q + \delta W^{int} = dU \quad (14)$$

which states that the change in internal energy is caused by heat interactions and coupled work interactions.

### **Energy conservation in a control volume**

The conservation of energy in a control volume can be derived considering a system with inlets and exits through which mass can flow.

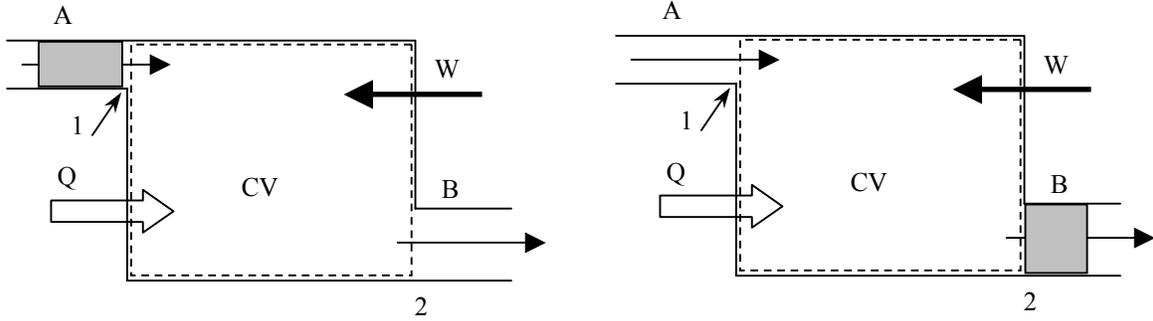
Consider the control volume shown in Fig. 1. At time  $t$  the control mass in consideration is the mass inside the control volume plus a small amount of mass  $m_{in}$  shown as A on the figure, and entering the CV through the control surface 1. At time  $t+dt$  the mass  $m_{in}$  is completely into the control volume and a mass  $m_{out}$  initially inside the CV has exited through the opening 2.

Since the time change  $dt$  is small we can write:

$$Q + W = E_{t+dt}^{CM} - E_t^{CM} = E_{t+dt}^{CV} + dE_{in} - E_t^{CV} - dE_{out} \quad (15)$$

and dividing by  $dt$  we get:

$$\dot{Q} + \dot{W} = \frac{dE_{CV}}{dt} + \frac{dE_{in}}{dt} - \frac{dE_{out}}{dt} \quad (16)$$



**Figure 1:** control volume used to derive the energy equation.

In Eq. (16) we calculate the rate of energy entering the CV as  $dE_{in}/dt = \dot{m}_{in} e_{in}$ , with a similar expression for the energy leaving. In addition, the work can be divided into shaft work, CV deformation work and the flow work. The two first terms are lumped together into the net work  $\dot{W}_{net}$ , and the third term is calculated as the work of the inflow and the outflow, or  $\delta W_{flow} = P v \dot{m} dt$ . Inserting the definitions in Eq. (16) we obtain:

$$\dot{Q} + \dot{W}_{net} + \dot{m}_{in} (Pv + e)_{in} - \dot{m}_{out} (Pv + e)_{out} = \frac{dE_{CV}}{dt} \quad (17)$$

In most applications the total energy can be well approximated with the internal, kinetic and gravitational energies only. In this case Eq. (17) reduces to:

$$\frac{dE}{dt} = \dot{Q} + \dot{W}_{net} + \sum_{in} \dot{m}_{in} \left( h + \frac{V^2}{2} + g z \right)_{in} - \sum_{out} \dot{m}_{out} \left( h + \frac{V^2}{2} + g z \right)_{out} \quad (18)$$

with the enthalpy already introduced in Eq. (3). A similar derivation leads to the mass conservation or continuity equation:

$$\frac{dm_{CV}}{dt} = \sum_{in} \dot{m}_{in} - \sum_{out} \dot{m}_{out} \quad (19)$$

In steady state all the time derivatives vanish, so the mass in must equal the mass out of the CV. This allows us to rewrite Eq. (18) as:

$$\dot{Q} + \dot{W}_{shaft} = \sum_{out} \dot{m}_{out} \left( h + \frac{V^2}{2} + g z \right)_{out} - \sum_{in} \dot{m}_{in} \left( h + \frac{V^2}{2} + g z \right)_{in} \quad (20)$$

A further simplification is possible when there is only one inlet and one exit:

$$\dot{Q} + \dot{W}_{shaft} = \dot{m} \left( h + \frac{V^2}{2} + g z \right)_{out} - \dot{m} \left( h + \frac{V^2}{2} + g z \right)_{in} \quad (21)$$

Other expression of interest is obtained multiplying Eq. (18) by  $dt$  and integrating in time to obtain

$$\Delta U_{CV} = Q + W_{net} + \int \left( h + \frac{V^2}{2} + g z \right)_{in} dm - \int \left( h + \frac{V^2}{2} + g z \right)_{out} dm \quad (22)$$

which relates the change in internal energy between the initial and final states of a transient process.

### **Homework**

Wark 1.32. A pressurized tank contains 0.1 kg of water vapor at 40 bar and 280 °C. Mass is allowed to flow out of the tank while heat is added, such that the temperature is maintained constant until the pressure reaches 10 bar. Determine the heat added in KJ, using a) constant enthalpy and b) approximating the data with a function and integrating.